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ADDITION REACTIONS AND PHOTOISOMERIZATION OF CIS,TRANS-1,5-CYCLODECADIENE

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by
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M.S., Louisiana State University, 1966
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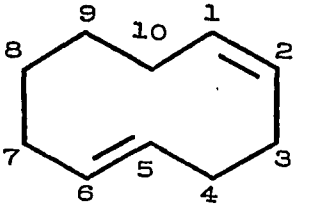
ABSTRACT

Ionic additions of reagents, such as trifluoroacetic acid, mercuric azide, acetonitrile, benzonitrile, molecular chlorine, iodobenzene dichloride, and bromine azide, to cis,trans-1,5-cyclodecadiene result in transannular cycloadditions to form substituted cis-decalins as products. The products from these reactions are consistent with stepwise or concerted mechanisms. The products obtained from the radical additions of halomethanes, molecular chlorine, iodobenzene dichloride, and bromine azide, which add to the diene by a stepwise mechanism, depend on the reagents and the conditions employed for the reactions. For poor transfer agents such as chloroform, and under very dilute conditions, the addition occurs exclusively by transannular (1,6) C-C bond formation. However, when a large excess of bromoform was used, some 1,2-addition product was also isolated. Carbenes generated from diazomethane, bromoform, and 5,5-dimethyl-N-nitrosooxazolidone also added to the diene. In each case, the carbene added to the trans double bond in the diene in preference to the cis double bond. The stereochemistry of some of these adducts, and the mechanistic implications of these results are discussed. Finally, the cis,trans-1,5-diene was photoisomerized to cis,cis-1,5-diene. The relative reactivities of these two isomeric dienes were compared by the Cope rearrangment and the addition of trifluoroacetic acid. The differences between the thermal stabilities and the reactivities of these two isomers are discussed in terms of conformational control of the transition states leading to the products.

CHAPTER I

INTRODUCTION

This study deals with ionic, radical, and carbene additions to cis,trans-1,5-cyclodecadiene (I) and with the photoisomerization of the diene.

I = 

Interest in these reactions derives from observations reported in the recent literature. For example, ionic addition of reagents to the diene I resulted in the formation of mono- or disubstituted cis-decalins; olefin addition reagents which can transfer atoms or groups to both olefinic carbons in one step add selectively to the trans double bond in both the diene I[1,2] and cis,trans,trans-1,5,9-cyclododecatriene;[3,4] and photoisomerizations of medium ring dienes do not follow a predictable pattern[5]. All these reports reflect the unusual properties of the medium ring compounds compared with other cyclic and acyclic olefins. In order to get more insight into the chemistry of I, the addition reactions with I have been extended to other reagents under both ionic and radical conditions. The list of other reagents includes some which can add to olefins by both mechanisms. Several carbenes were used to study the selectivities between cis and trans double bonds in the diene. The photoisomerization of I was also studied.

cis,trans-1,5-Cyclodecadiene belongs to the medium ring class of compounds (eight- to eleven-membered rings). These compounds have several physical and chemical properties which distinguish them from

other compounds. The most important of these distinguishing properties for olefins are the relative stabilities of the cis and trans isomers and transannular effects.[6]

In open chain olefins, the trans isomer is usually more stable than the cis isomer due to the fact that it has less steric interaction between the substituents. However, in alicyclic series, the relative stabilities of the cis and trans isomers depend on the ring size. Although no systematic data for the cycloalkadienes are available, quantitative data on the stabilities of the cis and trans cyclic olefins have been determined by direct equilibration[7] and heats of hydrogenation measurements.[8,9] These data are summarized in Table I.

TABLE I[7,8,9]

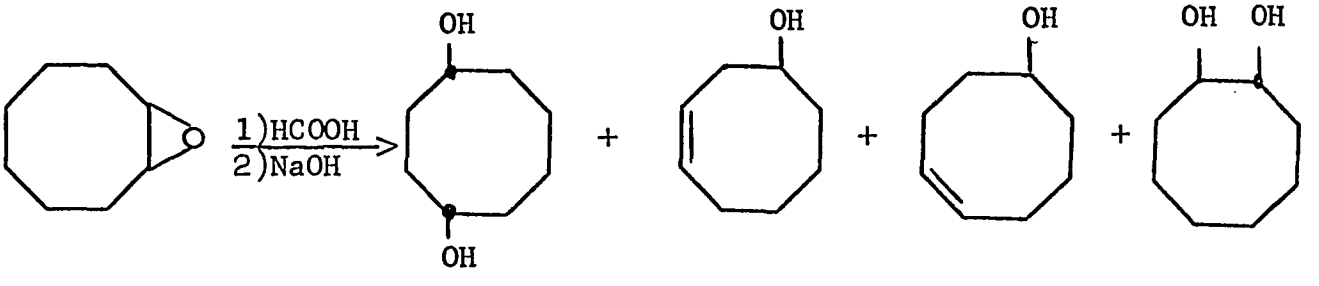
Thermodynamic Stabilities of Medium Ring Olefins

Ring Size	$\Delta(\Delta H^{o})$	$\Delta(\Delta G^{o})$	$K_{cis/trans}$	% cis
8	-9.26			
9	-2.87	-4.04	232	99
10	-3.34	-1.86	12.2	76
11	-0.12	0.67	0.406	29
12	-0.41	0.49	0.517	34

Here, $\Delta(\Delta H^{o})$ and $\Delta(\Delta G^{o})$ are the values of the differences of heats of hydrogenation and free energies of hydrogenation, respectively, of the cis- and trans-cycloalkenes. The instabilities of the trans double bond relative to the cis double bond in some of these olefins are reflected by their high heats of hydrogenation. The source of these instabilities includes angle strains (Baeyer strains). Thus, the high heat of hydrogenation reflects a high strain. As the ring size increases, the angle strain decreases. For ring sizes larger than ten,

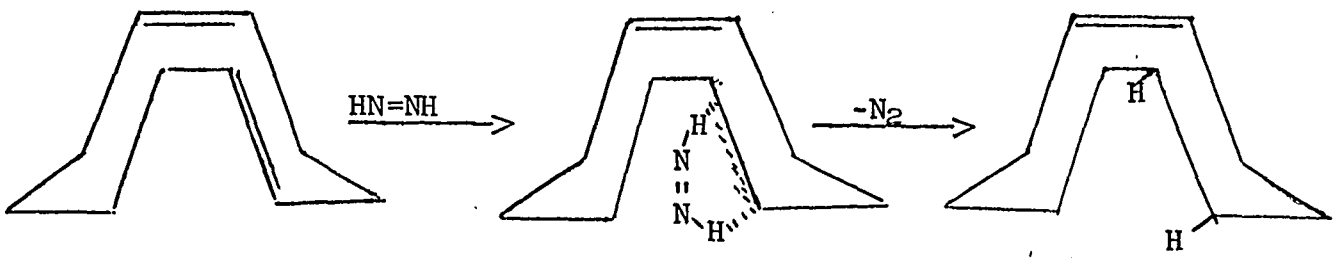
the trans double bond becomes more stable, and the factors which control the stabilities are substantially the same as for open chain olefins. Although data for the stabilities of cycloalkadiene are fragmentary, it is generally believed that the relative stabilities of cis and trans double bonds in the cycloalkadienes parallel those of the cis and trans double bonds in the corresponding cycloalkenes.

Another characteristic of the medium ring compounds is the transannular effects due to the proximity of the atoms or groups across the ring. Transannular hydride shifts were first discovered independently by A.C. Cope[10] and V. Prelog[11] and their coworkers. Since then many transannular reactions have been demonstrated.[6,12,13] Atoms or groups away from the original reaction site participate in a reaction, resulting in the formation of transannular products. For example,[14] the solvolysis of cis-cyclooctene oxide with formic acid followed by hydrolysis results in the formation of cis-1,4-cyclooctanediol, 3-cycloocten-1-ol, and 4-cycloocton-1-ol, in addition to the expected product, trans-1,2-cyclooctanediol.



The first three products can be explained by 1,3- or 1,5-hydride shifts in a cationic intermediate, followed by nucleophilic attack by solvent or by loss of a proton to form the products.

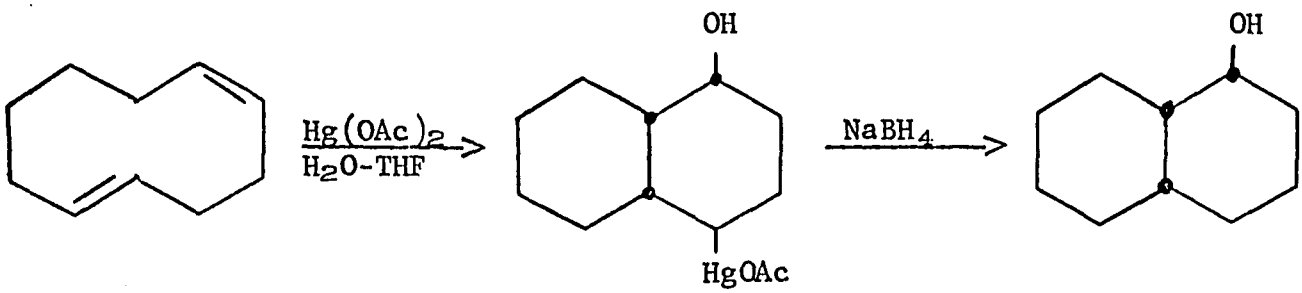
Recent investigations of the addition reactions of I[1] have provided some additional features of the characteristics of the medium ring compounds described above. Reaction of I with reagents which can transfer atoms or groups to both olefinic carbons in one step were shown to have a high degree of selectivity for the trans double bond in the diene. Reactions which were reported are diimide reduction,[1] diborane addition,[1] ozonation,[1] epoxidation,[1,2] and methyleneation.[1] It is believed that these reactions involve multicentered, concerted mechanisms, and both portions of the addends add to the double bond from the same side; that is, cis addition occurs. Diimide reduction of I, for example, may be pictured in the following way:



Other reactions of I involving principally the trans double bond of the diene are catalytic hydrogenations,[1] and 1 : 1 complex formation with gold(I) chloride.[15]

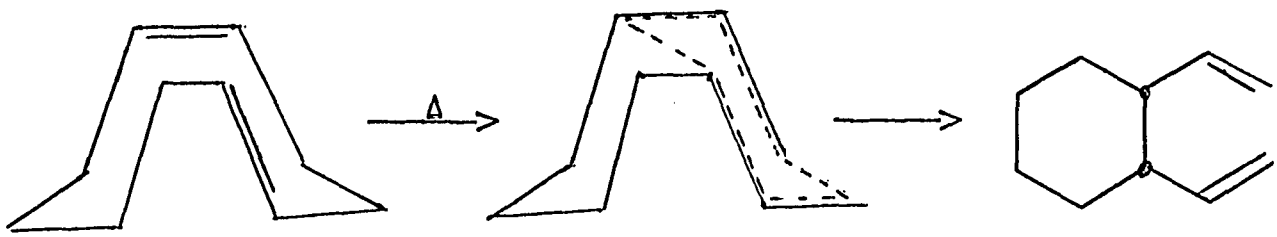
In contrast to the cis addition to the trans double bond described above, reactions of I with several ionic reagents, which add in steps, have been shown to involve both double bonds, and the products formed are 1,4-disubstituted cis-decalins.[1] Reagents which have been examined for ionic additions with I include bromine, lead tetraacetate, mercuric acetate, and methanesulfenyl chloride.[1] The addition of mercuric acetate to I in aqueous tetrahydrofuran solution followed by

sodium borohydride reduction to form cis-1-decalol as the major product is of special interest.



The formation of this alcohol is consistent with a mechanism involving initial attack at the trans double bond by the electrophilic species, participation by the cis double bond leading to transannular (1,6) C-C bond formation, and product formation by nucleophilic attack at position C-2 originally in the cis-double bond.

Other known reactions of I are the complexations with silver nitrate and copper halides (reactions were found to involve both double bonds),[16] photoisomerization to cis,cis- and trans,trans-1,6-cyclodecadienes with iron pentacarbonyl as catalyst,[17] and the thermal isomerization to cis-1,2-divinylcyclohexane.[18] The last reaction is an example of the Cope rearrangement and can be illustrated in the following manner:

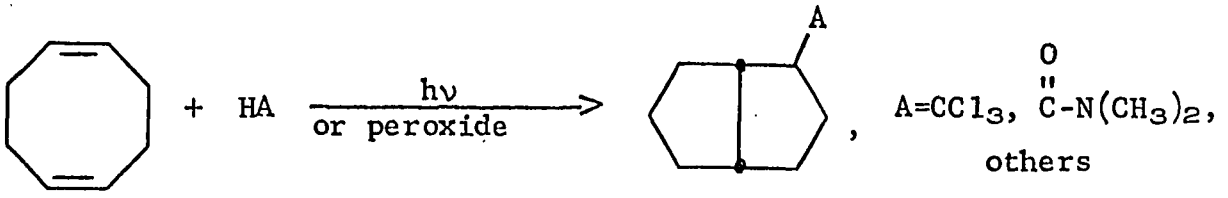


A six-membered ring transition state is depicted for this rearrangement.[18] Carbon atoms 1 and 6 are close to each other, and the relief

of internal strain in this medium ring compound may be the driving force for this transformation.

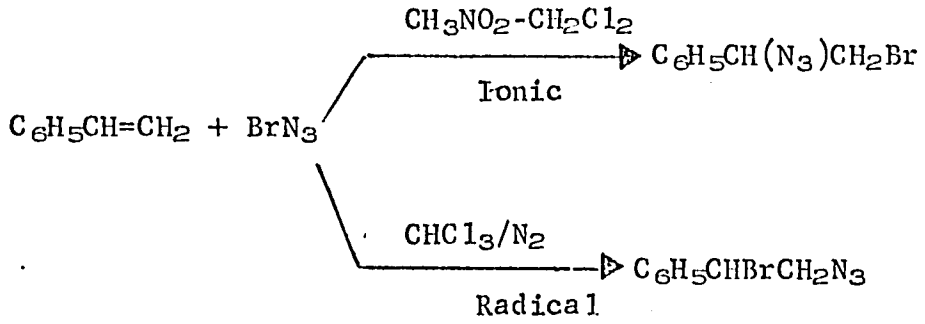
From the literature reviewed, it appears that both ionic and cis addition reactions with I occur preferentially at the trans double bond. In order to test the generality, and also for synthetic uses of I, these addition reactions with I have been extended to other reagents. If ionic reactions with I occur in general as in the reported cases,[1] one may use I as the starting compound to synthesize mono- or disubstituted cis-decalins with known stereochemistry by using appropriate addition reagents. Reagents used for this study include trifluoroacetic acid, chlorine, iodobenzene dichloride, bromine azide, mercuric azide, and acetonitrile and benzonitrile in the presence of sulfuric acid. Several carbenes generated from diazomethane, bromoform, and 5,5-dimethyl-N-nitrosooxazolidone were used to compare these reactions with the known methyleneation reaction employing methylene iodide and zinc-copper couple.[1]

Another interest of this study was the investigation of possible transannular cycloadditions of I under free radical conditions. Initial examples of transannular reactions were associated with carbonium-ion processes.[12,19] However, several radical transannular reactions have recently been reported.[20,21,22] For example, radical addition of reagents to cis,cis-1,5-cyclooctadiene gave derivatives of bicyclo[3.3.0]octane.[22]



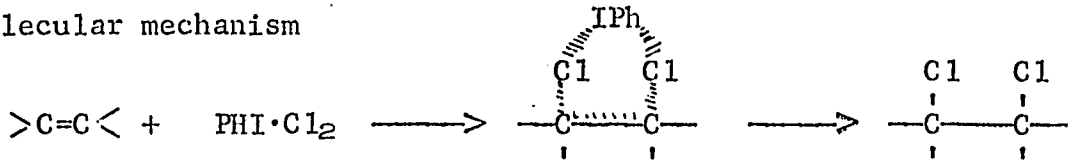
I reacts with many ionic reagents mentioned before much faster than does cis,cis-1,5-cyclooctadiene, and only transannular products were formed. These comparisons suggest that the tendency for (1,6) C-C bond formation with I might be greater under the same conditions than with 1,5-cyclooctadiene. Therefore, reactions of I with halomethanes, bromine azide, molecular chlorine, and iodobenzene dichloride, all radical addition reagents, were carried out.

It should be pointed out here that some of the reagents, such as bromine azide, molecular chlorine, and iodobenzene dichloride were used for both ionic and radical additions with I, allowing comparisons between ionic and radical processes involving the same addends. Bromine azide appears to be the ideal reagent for this purpose, because it can play alternate roles in the addition reactions with olefins, depending upon the polarity of the solvent.[23] Thus, in nitromethane-methylene chloride solution, bromine azide added to styrene to give the Markovnikov product, while in chloroform with the exclusion of air, the anti-Markovnikov product was formed.[23]

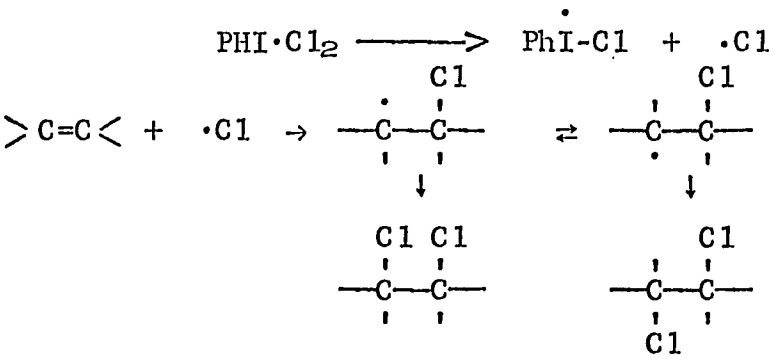


The addition of chlorine to olefins by use of iodobenzene dichloride as a halogenating agent has received attention from several research groups.[24] In some cases, both cis- and trans-dichlorides are formed. Two mechanisms, namely molecular addition,[25] and free radical chain processes,[24] have been proposed to explain the results. The following scheme outlines the mechanisms proposed to account for the cis-product.

Molecular mechanism



Radical mechanism



I has been used here as a reagent for probing the reaction mechanism. If the reaction proceeds by the molecular addition mechanism, cis-1,2-addition would be expected from the reported behavior of I. On the other hand, a free-radical chain process would be expected to give quite different products.

The final part of this thesis deals with the possible photoisomerization of I. Photochemical cis-trans isomerizations of olefins can be effected by direct or sensitized irradiation with light. Frequently, the isomer of lesser ground state stability is formed in the higher yield because of the energy difference between the cis and trans triplet states in cis-trans isomerization reactions.[26] However, the photochemical behavior of medium ring dienes is somewhat unpredictable.[5] For example, several photoisomerizations of cyclooctadienes and cyclodecadienes have been reported. In some cases, geometrical and/or positional isomerization of one or both C=C occur; in some, intramolecular cycloaddition to form cyclobutane derivatives occur; and with cis,-cis-1,5-cyclooctadiene, intramolecular cycloaddition occurs in a "crossed" fashion to produce tricyclo[3.3.0.$0^{2,6}$]octane. The structural features responsible for the rather individual behavior of each cyclic diene have not been clearly identified. Therefore, a study of this photochemical transformation is also inviting.

CHAPTER II

RESULTS AND DISCUSSION

In this chapter the results of the reactions of I will be reported and discussed, first the addition reactions, and then the photoisomerization of I. A comparative study of the relative stabilities and reactivities of cis,trans- and cis,cis-1,5-cyclodecadienes will be included, also.

Addition Reactions

The addition reactions of I are grouped and discussed under the following classifications: 1) ionic, 2) radical, 3) ionic and radical, and 4) carbene additions. As pointed out in the earlier chapter, the main interest in the ionic and radical addition reactions has been the stereochemical results, the reaction mechanisms and the differences between these two processes. The interest in the carbene additions lies in the selectivities of reactivities of the cis and trans double bonds in the diene I toward various carbene species.

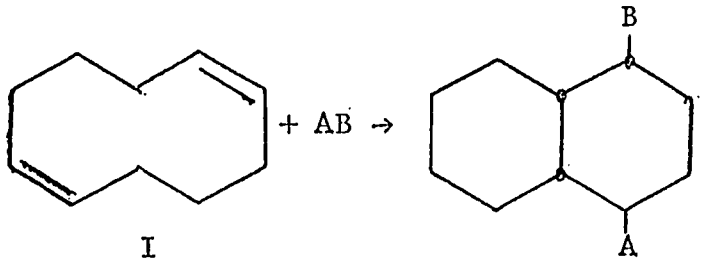
Ionic Addition

The reactions of I with several ionic addition reagents involved transannular cycloaddition to form substituted cis-decaline as major products. These results are summarized in Table II.

TABLE II

Substituted cis-Decalins from Ionic Reaction of I

Addition Reagent	Product	Yield(%)
CF_3COOH	cis-1-trifluoroacetoxy-cis-decalin (II)	90
$Hg(N_3)_2$	cis,cis-1-decalol (III, 11%) cis-1-azido-cis-decalin (V, 39%) VI (1.2 g)	60-70
CH_3CN/H_2SO_4	N-(cis,cis-1-decahydronaphthyl)-acetamide (VII)	64
C_6H_5CN/H_2SO_4	N-(cis,cis-1-decahydronaphthyl)-benzamide (VIII)	58



I

II, A=H, B=$OCOCF_3$

V, A=H, B=N_3

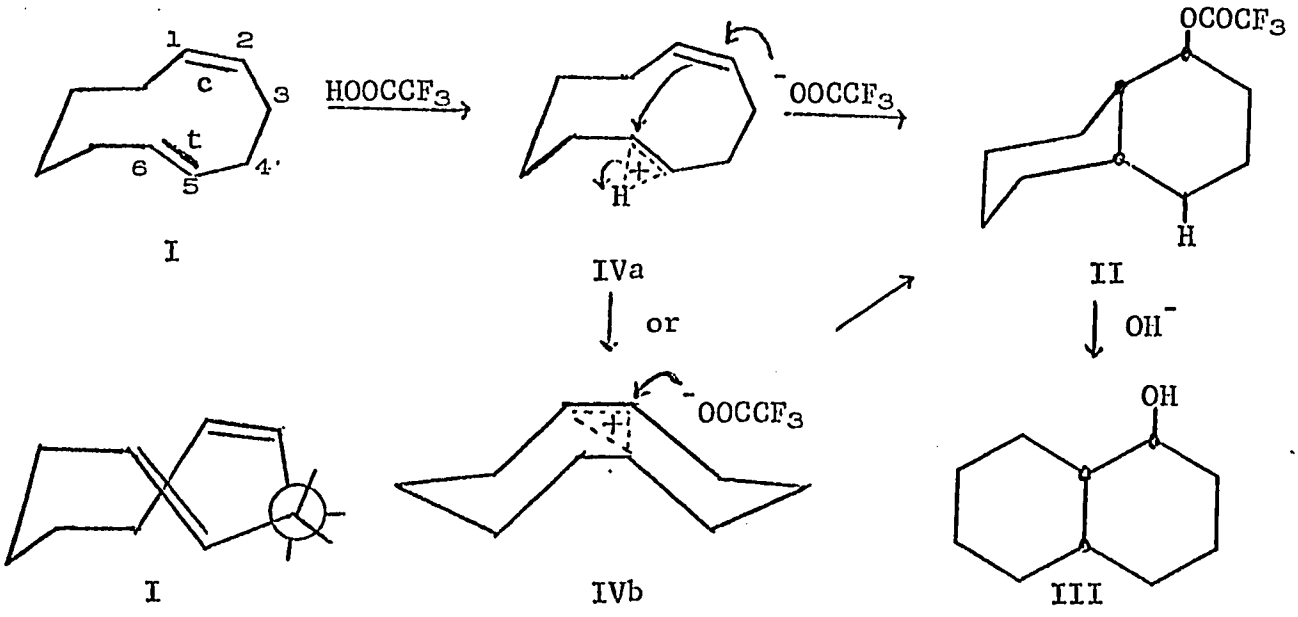
VII, A=H, B=$NHCOCH_3$

VIII, A=H, B=$NHCOC_6H_5$

When I was added to trifluoroacetic acid, an exothermic reaction occurred. The product, formed in greater than 90% yield, was cis-1-trifluoroacetoxy-cis-decalin (II), b.p. 99-100.5°C (9 mm). The structural assignment was based on the nuclear magnetic resonance (nmr) and infrared spectra. The infrared spectrum of II (Fig. 1) included absorption at 5.57 μ, indicative of the presence of trifluoroacetoxy group. The nmr spectrum of II (Fig. 2) consisted of a multiplet at -5.0 ppm (1H, C<u>H</u>O$COCF_3$) and a broad multiplet between -1.0 and -2.0 ppm (16H, cis-decalin framework). Further verification of the structure and stereochemistry of II was done by basic hydrolysis of II to the corresponding alcohol III (m.p. 90-91°C).[27] The infrared and nmr spectra of the alcohol were identical with those of an authentic sample.[28]

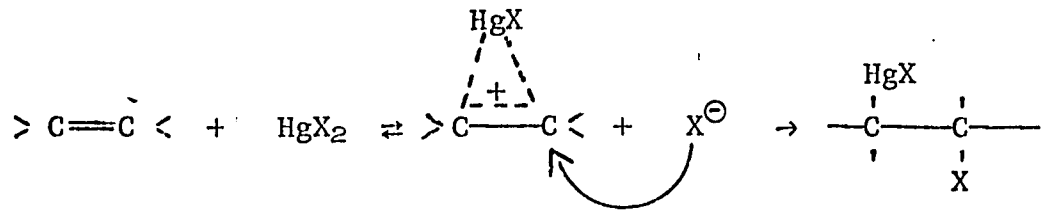
The formation of such a transannular cycloaddition product is not surprising in view of the reported ionic addition reactions with I. The striking fact is that the trifluoroacetoxy group is trans to the vicinal proton at the ring junctures. If one adopts the proposed mechanism[1] (Scheme I) or a bridged intermediate (IV_b), the result can be readily explained. The initial attack by the cationic species (H^+) occurs at the trans double bond of the diene to form a π-complex (IV_a) or a bridged carbonium ion (IV_b); subsequently, nucleophilic attack (B^-) at position C-2 gives product (II). If the initial attack by proton were to occur at the cis double bond and the subsequent attack by nucleophile were to occur at C-5 (both attacks with the same orientation as those in the first description), the product formed would be <u>trans</u>-1-trifluoroacetoxy-<u>cis</u>-decalin.

Scheme 1

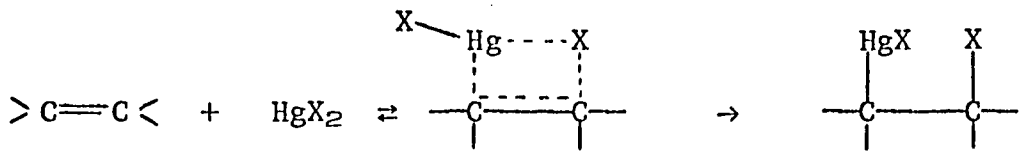


Two questions remain to be answered: 1) What is the driving force for this transformation? 2) If the proposed mechanism is operating, what factor directs the initial attack by electrophile to the trans double bond? The first question is not so hard to answer. The conversion of the 1,5-cyclodecadiene to a substituted cis-decalin is accompanied by substantial strain relief as large C-C bond angles in the ten-membered ring change to normal tetrahedral angles. The answer to the second question is not so obvious. The relative strain of the cis and trans double bonds in the diene or the relative degree of steric interactions in the transition state might well be the factor in determining the direction of the addition reactions.

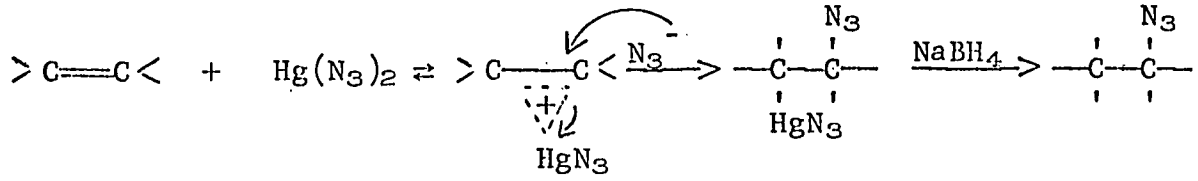
Electrophilic addition of mercury(II) salts to olefins have received much attention from organic chemists in recent years.[29,30] Mercury salts react with olefins to yield trans addition products in some cases and cis addition products in the others. Therefore some concern has arisen as to the mechanisms of the addition reactions. Trans addition is generally attributed to the formation of a three-membered ring, cationic intermediate by reaction between the π-electrons of the olefin and the electrophile, followed by attack of the nucleophile at the carbon atom at which the positive charge would be the more stabilized.[31]



When an exclusively cis addition is observed, a four-centered mechanism is frequently proposed.[32] Thus cis and trans addition products appear to require different mechanisms.



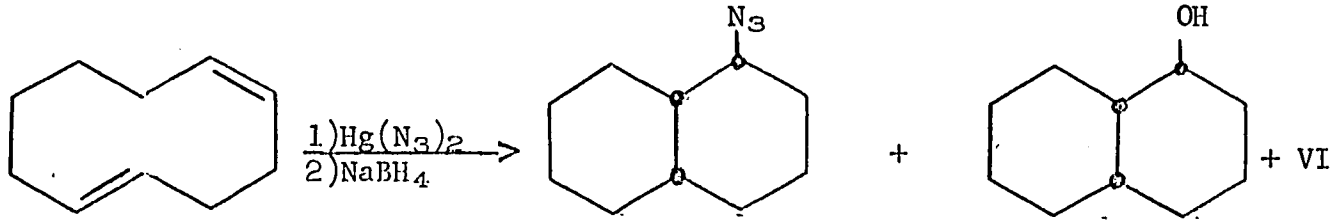
Mercuric azide reacts with terminal alkenes or strained cyclic alkenes to yield β-azidoalkylmercurials[33], which may be reduced in situ by sodium borohydride to yield alkyl azides.[34] An ionic intermediate mechanism is proposed.[33]



Although the mechanism is strongly supported by the observation that $k_{N_3^-}/k_{H_2O}$ increases greatly with increasing delocalization of a cation, a direct chemical test is desirable. That I reacts with many ionic reagents by a stepwise mechanism to give the substituted cis-decalins,[1] and with other reagents by concerted, cis-addition mechanisms to give 1,2-addition products[1] suggests that I may be a suitable reagent for probing the reaction mechanism.

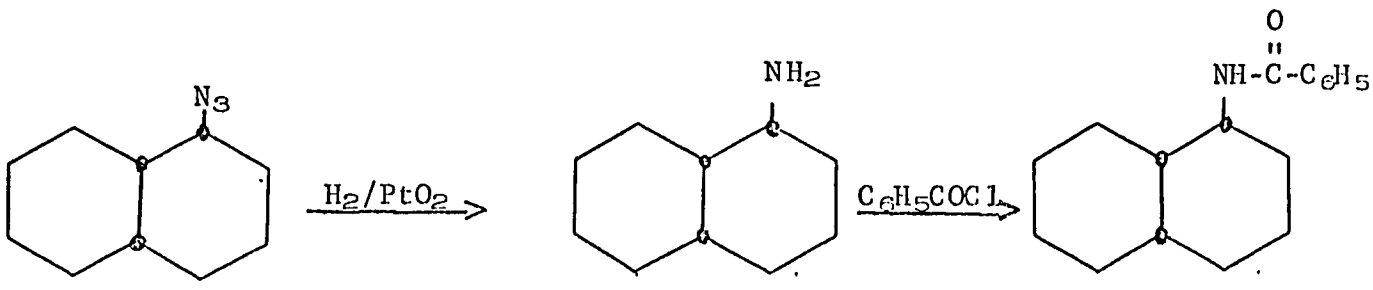
When I was mixed with mercury(II) azide in 50% aqueous tetrahydrofuran solution, reaction proceeded smoothly without heating. The alkylmercurial derivatives formed in this reaction were not isolated;

instead, they were demercurated *in situ* by sodium borahydride. The product mixture was separated by column chromatography on Merck alumina (acid-washed) with petroleum ether, ether, and methanol to give *cis*-1-azido-*cis*-decalin (V, 11%), *cis*,*cis*-1-decalol (III, 39%), and an unidentified compound (VI).



I V III

The structural assignment for V was based on the spectroscopic data. The infrared spectrum of V (Fig. 3) has absorption at 4.75μ, characteristic of an azido group. The nmr spectrum of V (Fig. 4) consisted of a multiplet at -3.45 ppm (1H, C<u>H</u>N_3), and a broad multiplet between -1.0 and -2.1 ppm (16H, *cis*-decalin framework). Further verification of the identity of the compound was accomplished by catalytic hydrogenation of the azide to the amine (VII).[35] Since reduction of azide to amine occurs with retention of configuration,[36] the stereochemistry of the substituent should remain the same. The benzoyl derivative of the amine VII had melting point 205-206°C, corresponding to that of the known compound, N-(*cis*,*cis*-1-decahydronaphthyl)-benzamide (VIII, lit. m.p. 206°C).[27]

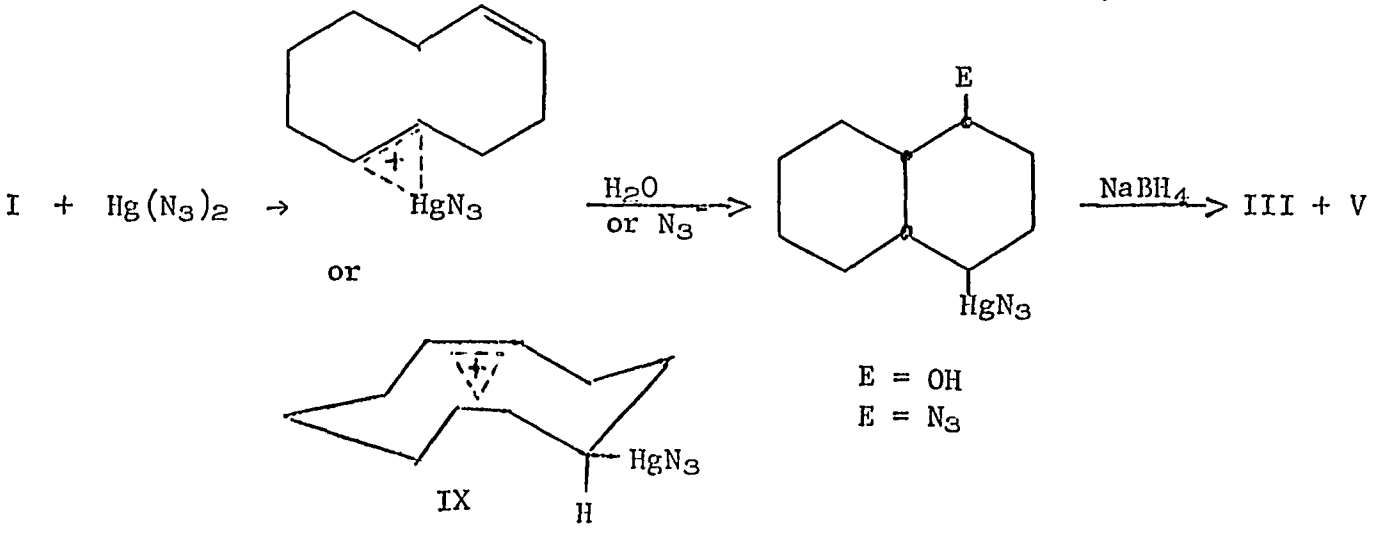


V VII VIII

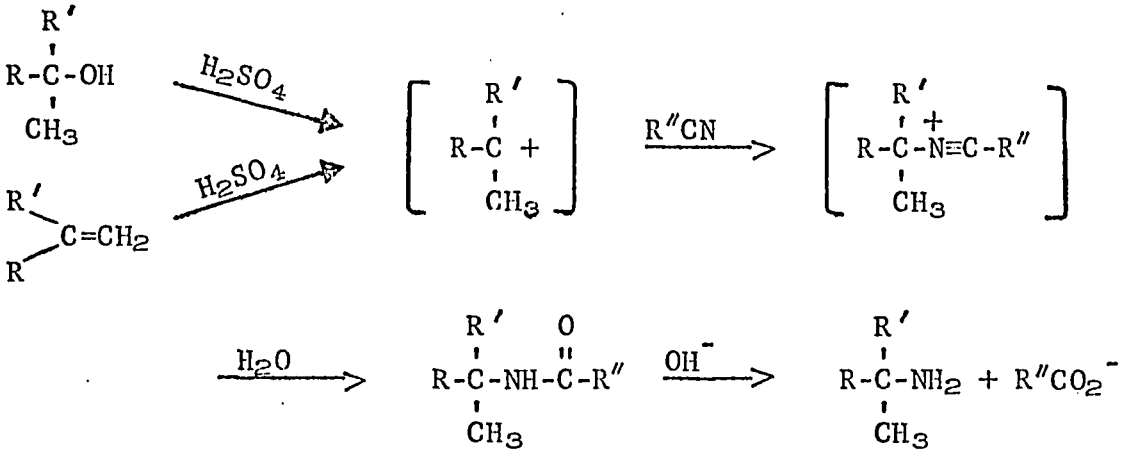
The structure of VI has not been established, however, the infrared spectrum of VI included strong absorption at 4.75μ, indicative of the presence of azido group, and no absorption at wavelength lower than 3.4μ attributable to C=C-H stretching vibrations or due to the presence of a hydroxyl group. The nmr spectrum of VI consisted of multiplets centered at -3.36 ppm, and between -1.0 and -2.2 ppm; the ratio of these two areas was about 1:4. From these data one can only conclude that VI is a saturated compound derived from I with an azido substituent in the structure.

The result of this reaction indicates that the reaction does not proceed by a four-center reaction mechanism. A concerted, four-center mechanism would presumably lead to 1,2-addition product, which was not observed in this reaction. The formation of III and V in the process implies that the azide anion and the solvent, water, compete with each other for the cationic intermediate IX. The mechanism used to illustrate the addition of trifluoroacetic acid may be applied here also (Scheme 2).

Scheme 2



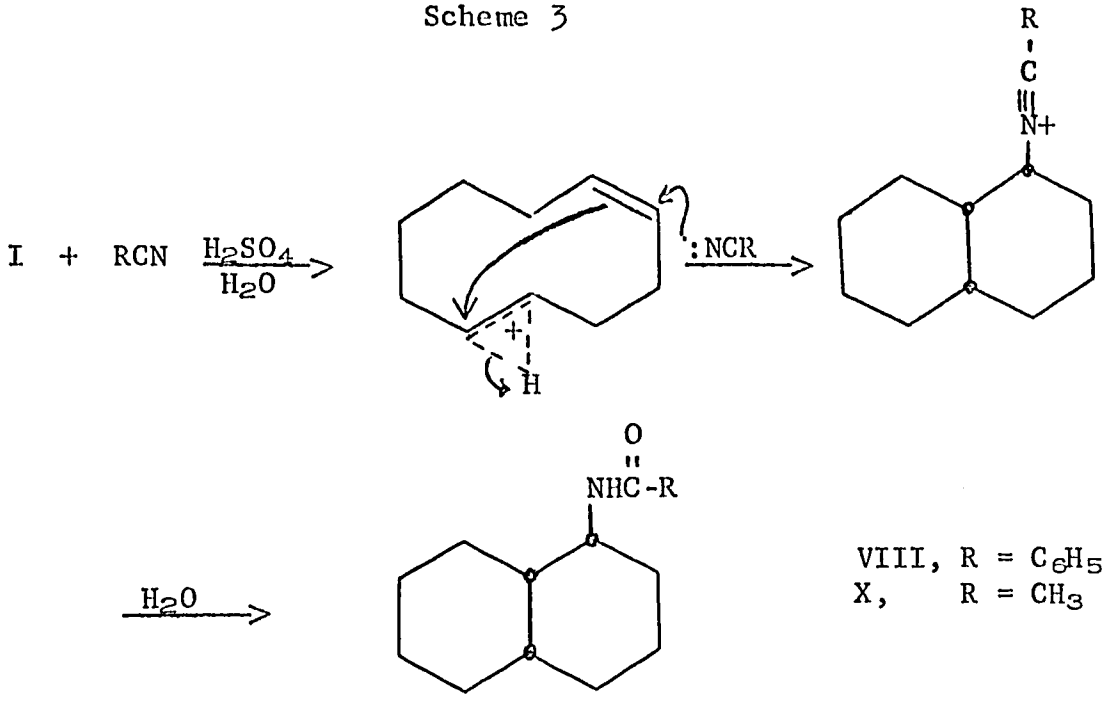
Another reaction studied under the ionic additions was the "Ritter Reaction".[37] This reaction between alkenes or alcohols and nitriles is an important method for preparing tertiary alkylamines or amides. It is restricted to alcohols and alkenes that can form relatively stable carbonium ions.



The reaction in the case of alkenes involves protonation in the initial step followed by the attack by the nitrogen in the nitrile group and subsequent hydrolysis to give the product. The tendency of I to form cis-decalin derivatives when reacted with protonic acid suggested that this reaction might be a useful means of preparing cis-decalylamine or its amide under very mild conditions.

Reaction of I with acetonitrile and with benzonitrile in the presence of concentrated sulfuric acid indeed gave N-(1-decahydronaphthyl)-acetamide (X)[27] and N-(1-decahydronaphthyl)-benzamide (VIII)[38] respectively. More interestingly, the major products isolated were formed stereoselectively; the substituted cis,cis-1-decalylamine structures were confirmed by the infrared and nmr spectra and the physical properties of the compounds. Again, a mechanism such as the one shown in scheme 1 may be applied here (Scheme 3).

Scheme 3



VIII, R = C_6H_5
X, R = CH_3

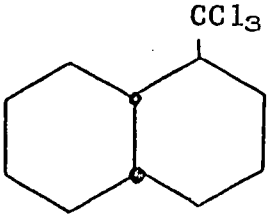
From these ionic addition reactions, it appears that I reacts with protonic acids, and with mercury(II) salts by similar if not identical mechanisms. These reactions provide a convenient method for the synthesis of cis,cis-1-decalyl derivatives.

Radical Addition

Although ionic additions of reagents to I frequently lead to transannular cyclization products,[1] the corresponding radical cycloadditions had not been investigated prior to this study. The study of radical additions of polyhalomethanes to be presented here provides the first example of a free-radical cycloaddition in the cyclodecadiene series.

The reaction of I and chloroform initiated by ultraviolet light (2537 Å) resulted in the formation of transannular cycloaddition products. The reaction mixture was shown by gas chromatography to consist of one major product (66 area %) three components with shorter retention time than the major product (18% total), and some high boiling,

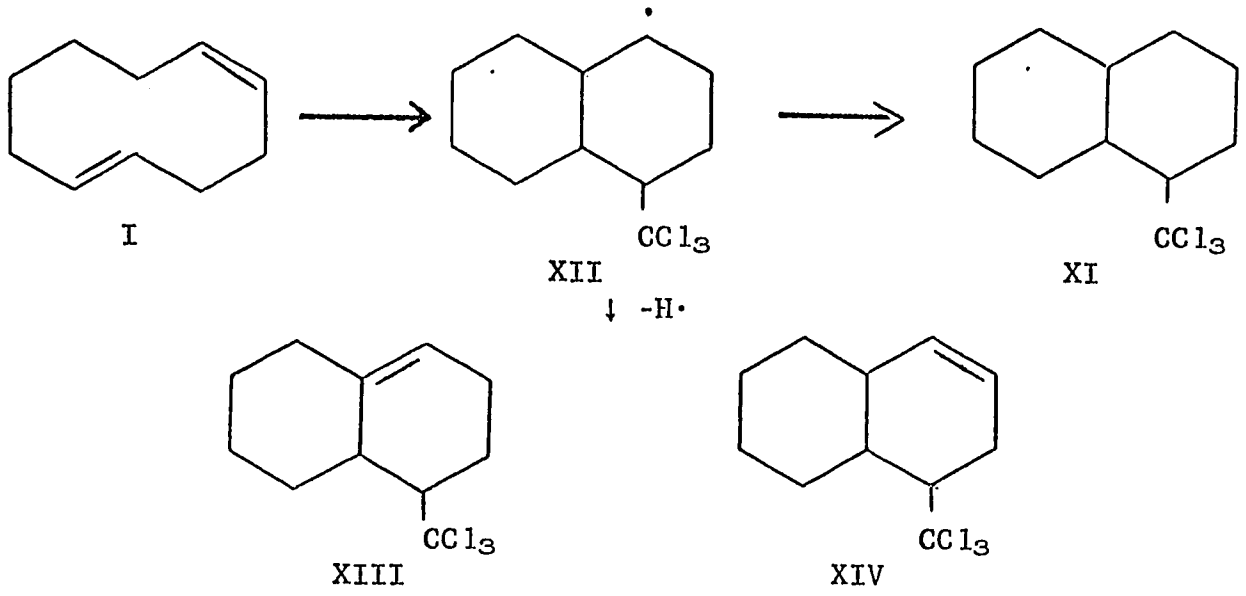
long retention time materials (12%). The major product (XI) was separated by fractional distillation (b.p. 90-92.5°C, 0.6 mm) and purified by gas chromatography. The adduct XI was characterized as 1-trichloromethyl-cis-decalin on the basis of the following spectroscopic data and chemical evidence.



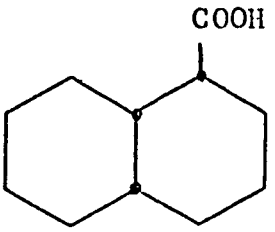
XI

The infrared spectrum of XI (Fig. 5) included strong absorptions at 12.8 to 13.0 μ, indicative of the presence of a trichloromethyl group, and no absorption at wavelength lower than 3.4 μ, attributable to C=C-H stretching vibrations. The nmr spectrum of XI (Fig. 6) consisted a multiplet centered at -2.70 ppm (1H, $C\underline{H}Cl_3$), and a complex multiplet between -1.0 and -2.5 ppm (17H, the rest of the ring protons). The compound did not decolorize aqueous potassium permenganate or bromine in carbon tetrachloride solution. The absence of olefinic linkage in the compound XI and the tendency of the formation of C-C bond between C-1 and C-6 in the ionic addition reactions with I strongly suggest that the structure of XI is 1-trichloromethyl-cis-decalin. The minor products were not studied in detail. It was assumed that the shorter retention time components, present in fraction 3 of the distillate were derived from the intermediate radical (XII) by loss of a hydrogen atom to form products such as 4-trichloromethylbicyclo[4.4.0]dec-1-ene(XIII) and 4-trichloromethylbicyclo[4.4.0]dec-2-ene (XIV) (Scheme 4).

Scheme 4

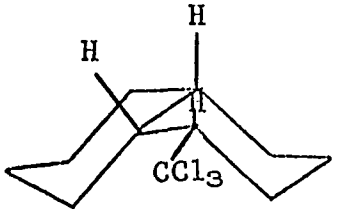


The stereochemistry of XI has not been firmly established. One way of establishing the stereochemistry at the ring juncture of XI is to convert XI to a known compound such as decahydronaphthoic acid, because the isomers of the acid with cis or trans ring juncture have distinctive physical properties, such as melting point, and differ in their infrared and nmr spectra. The hydrolysis of XI with potassium hydroxide in a mixed solvent yielded an acid whose nmr spectrum consisted of a broad signal at -11.8 ppm (1H, -COO<u>H</u>) a multiplet at -2.28 ppm (1H, C<u>H</u>COOH), and another multiplet between -1.0 and -2.0 ppm (16H, the rest of the ring protons). The infrared spectrum included absorption at 5.87 μ, characteristic of the carboxylic acid functional group. The upfield absorptions (-1.0 to -2.0 ppm) in the nmr spectrum of the acid derived from XI were similar to those of the monosubstituted <u>cis</u>-decalin, suggesting <u>cis</u>,<u>cis</u>-1-decahydronaphthoic acid (XV) as the possible product.

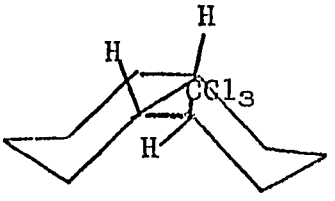


XV

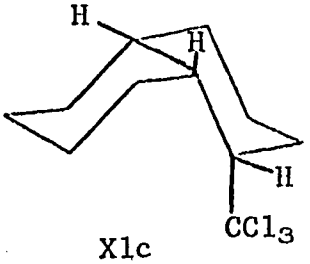
The stereochemistry of the trichloromethyl group in XI remains to be determined. The reason is that the acid XV could have been derived from the cis,cis-1-trichloromethyldecahydronaphthalene, but the trans, cis-isomer can also give the same product by way of isomerization at the C-1 position of the acid. However, it is reasonable to assume that the bulky trichloromethyl group in XI occupies the equatorial position (XIa or XId), where it has the least steric interactions, rather than the axial isomers such as XI_c or XI_b. XI_c and XI_b are energetically unfavorable as compared with the equatorial isomers due to the nonbonding interactions between the axial hydrogen atoms and the trichloromethyl group.[39]



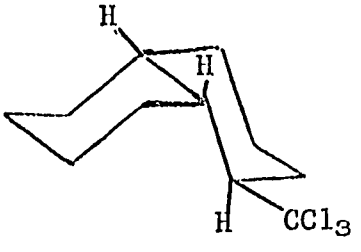
XIa



XIb

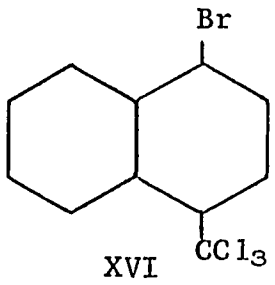


XIc



XId

Reaction of I with excess bromotrichloromethane, with 3500 Å lamps being used to initiate the radical addition reaction, proceeded quite smoothly and was complete within one hour. The nmr spectrum of the reaction mixture consisted of two sets of sextet signals centered at -4.46 ppm and -3.92 ppm, (relative intensities, 1 and 1.4 respectively), absorptions in the olefinic region (-5 to-6 ppm) and absorptions between -1.0 and -2.80 ppm. Distillation of this mixture gave 17 g of slightly yellow liquid, which solidified upon cooling to room temperature. Recrystallization of the solid material from pentane yielded 15 g of the major adduct (XVI) which melted at 67-69°C.

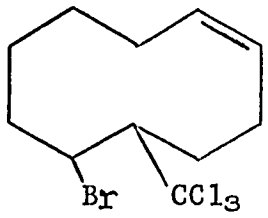


XVI

The infrared spectrum of XVI (Fig. 7) includes strong absorption at 12.8 and 13.5 μ, indicative of the presence of the CCl_3 group. The nmr spectrum of XVI (Fig. 8) includes a sexted at -3.92 ppm (1H, C<u>H</u>Br), a multiplet at -2.65 ppm (1H, C<u>H</u>-CCl_3), and a complex multiplet between -1.0 and -2.5 ppm (16H, the rest of the protons). The structure of XVI is, therefore assigned as 1-bromo-4-trichloromethyl-<u>cis</u>-decalin on the basis of the spectroscopic data and analogy to the chloroform addition reaction with I. Two minor products were detected in the second fraction of the distillation. Separation of the original mixture elution chromatography also led to the isolation of XVI as major product in the middle collections. In the early collections, two minor products were present;

and in the latest collections, a component was obtained in small amounts.

The two minor products mentioned above were detected but not firmly identified. Gas chromatographic analyses showed that they had the same retention times as the minor products obtained from the radical addition of chloroform to I. Therefore, the structures of these two components are assigned as XIII and XIV. Another component obtained in small amounts in the latest collections from the elution chromatography gave spectra consistent with the structure, 5-trichloromethyl-6-bromo-cis-1-cyclodecene (XVII).



XVII

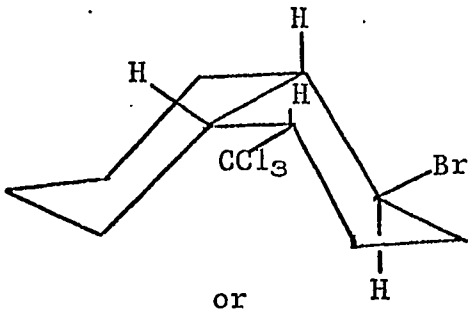
It was noted that the nmr spectrum of the initial $BrCCl_3$ reaction mixture included also a sextet signal centered at -4.46 ppm not yet assigned to identified products. This absorption is attributable to an equatorial proton geminal to bromine atom in the cyclohexane ring system,[40] and many attempts were made to isolate the compound for further study. Unfortunately, all attempts failed. Decomposition, revealed by the liberation of hydrogen bromide, occurred during distillation. Elution chromatography using florisil or alumina resulted in product which gave no -4.46 ppm signal. When a sample of the reaction mixture was treated with half an equivalent of potassium hydroxide in a mixed solvent, the signal at -4.46 ppm disappeared completely, and increased absorption appeared in the olefinic region of the resulting nmr spectrum.

Because of the possible existence of XVIII, a stereoisomer of XVI, in the reaction mixture, and in order to understand more detail of the radical addition reactions with I, the addition of bromotrichloromethane to I was carried out in dilute methylene chloride solution. The relatively poor chain transfer property of the methylene chloride under these conditions enables one to study the product distributions as a function of concentration. When a 1 : 1 mixture of I and bromotrichloromethane in methylene chloride solution was irradiated by 3500 Å lamps as before, the reaction proceeded smoothly and was complete in 3.5 hours. After removal of the solvent, the nmr spectrum of this reaction mixture was taken and compared with the nmr spectrum obtained from the previous mixture formed in excess bromotrichloromethane. The nmr spectra of these two product mixtures contained some interesting features. Both spectra included sextet signals at -3.92 ppm and -4.46 ppm, but the relative intensities of these signals were different in the two spectra. The ratio of the intensities (-4.46 to -3.92) was 1 : 1.4 for the excess bromotrichloromethane reaction, and was 1 : 4 in the dilute methylene chloride one. There was also, surprisingly, more intense olefinic absorption in the excess bromotrichloromethane mixture than in the dilute methylene chloride one.

At this point, the stereochemistry of the bromo and trichloromethyl groups in XVI and its stereoisomer, XVIII, and the implication of the concentration effect on the product distributions from the reactions described above will be considered.

The chemical shift of the sextet signal at -3.92 ppm in XVI is in the range of an axial proton geminal to a bromine atom in a cyclohexane

ring system.[40] Therefore, the bromine is equatorial. Further support for the argument that bromine occupies an equatorial position comes from the vicinal splitting pattern of the proton under consideration. From Fig 8, it can be seen that the sextet signal consists of a small coupling of 2.5 Hz and large couplings of 9.5 Hz. These constants are consistent only with an axial proton coupling with an equatorial proton ($J_{axial-equatorial}$=2-6 Hz) and with two axial protons ($J_{axial-axial}$=8-13 Hz) to give the observed sextet signal. For the trichloromethyl group, the same argument used for the assignment of the structure XI may be applied here. In other words, the bulky trichloromethyl group also occupies an equatorial position. From these considerations, the two substituents are trans to each other, and the complete structure of XVI is assigned as illustrated.



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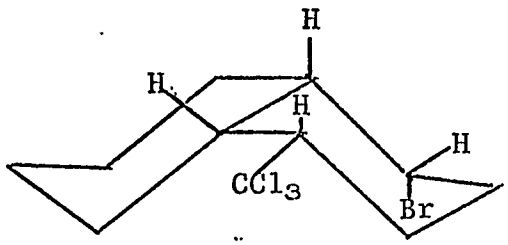

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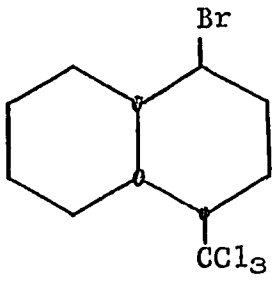
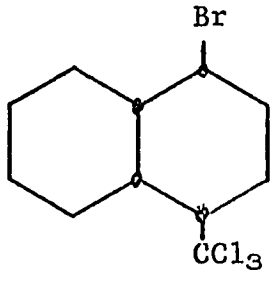


XVI

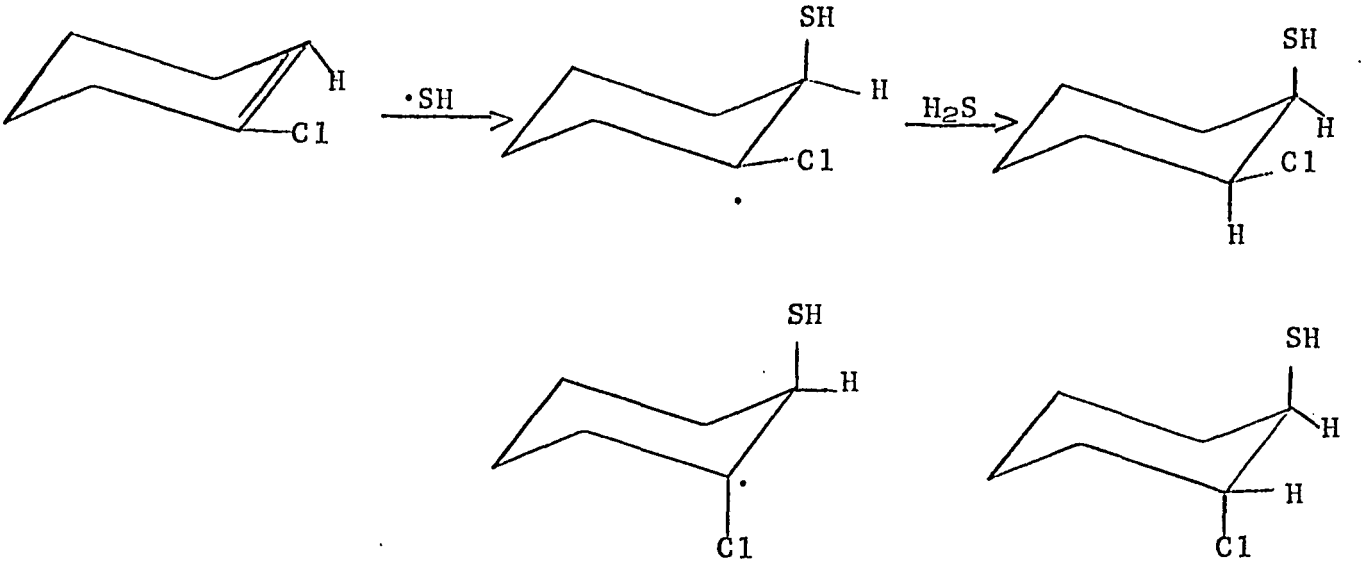


XVIII

Following arguments similar to those above, compound XVIII is best represented by the structure shown above. This structure not only explains the observed small splitting with the neighboring protons for the proton but also accommodates the instability of the bromide to heat or base. The trans coplanarity between the axial protons and the axial bromine atom is an ideal situation for elimination to alkene.

The change of product distributions in the radical additions of bromotrichloromethane to I with concentrations requires more consideration. The fact that more unsaturated compounds were formed at high bromotrichloromethane concentrations can be explained by the hydrogen atom abstractions by the trichloromethyl radicals. At higher bromotrichloromethane concentration, more trichloromethyl radicals are present; therefore, the chance for the hydrogen atom abstractions is greater than when fewer trichloromethyl radicals are available. This proposal requires the formation of chloroform in the reaction mixtures. In fact, chloroform was detected by both gas chromatographic and nmr spectral analyses of the reaction mixtures. The increase in the production of XVI and the decrease in XVIII as the concentration of bromotrichloromethane decreases follow from the nature of concentration effects on radical addition reactions. In radical additions, the concentration effects on the geometrical isomer distributions have been attributed to the transfer rate and the interconversions between intermediate radicals.[41] For example,[42] the addition of hydrogen sulfide to 1-chlorocyclohexene has been shown to give high stereoselectivity (cis product) at high hydrogen sulfide concentrations. The argument here is that the initially formed radical is trapped by the hydrogen sulfide before it has time to convert to another radical conformer. At low hydrogen sulfide concentrations,

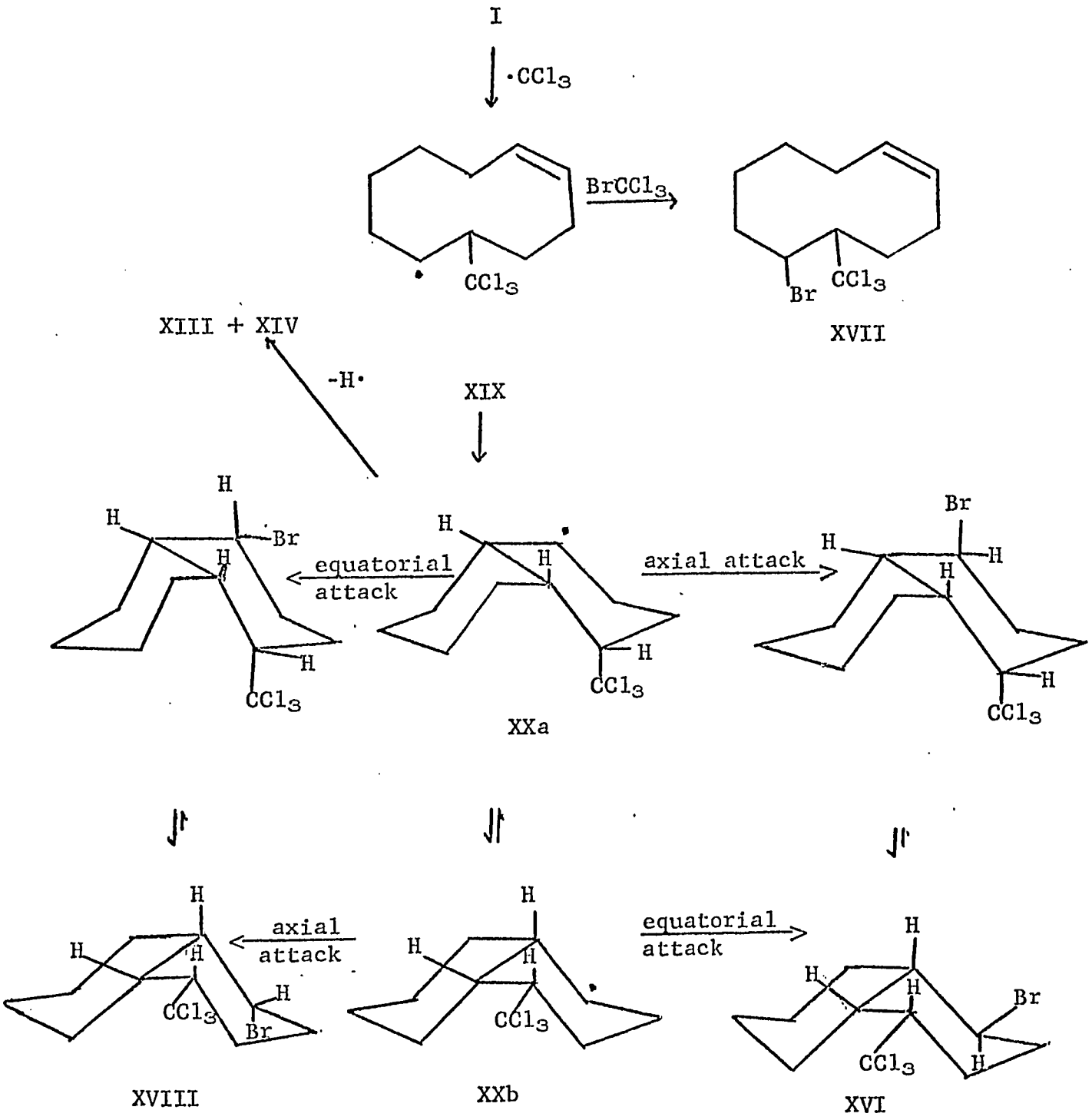
the transfer rate is slow, allowing time for the two intermediate radicals to interconvert to give the products non-stereoselectively.



Although the scheme here illustrates diaxial attack, a diequatorial attack mechanism can also explain the results as well.

With these consideration in mind, a mechanism which could account for the experimental results for the radical additions of bromotrichloromethane to I is proposed (Scheme 5).

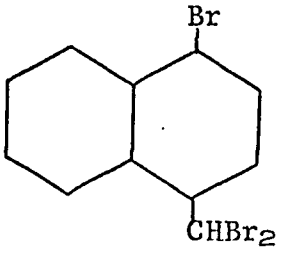
Scheme 5


I
·CCl3
BrCCl3
CCl3
Br
CCl3
XVII
XIII + XIV
-H·
XIX
H
H
Br
H
equatorial
attack
H
H
H
CCl3
axial attack
Br
H
H
H
H
CCl3
XXa
H
H
H
axial
attack
H
CCl3
Br
H
H
H
CCl3
equatorial
attack
H
H
Br
H
CCl3
XVIII
XXb
XVI

In this mechanism, the initial attack on I by the trichloromethyl radical comes either at position C-2 or at C-5 to form an intermediate radical (XIX), which then undergoes transannular cycloaddition to give another intermediate radical, XX_a. XX_a may be in equilibrium with XX_b. Loss of proton from either side of the radical center of XX would give the olefinic products, XIII and XIV. The product distributions between XVI and XVIII are then determined by the transfer rate of bromine atom at the axial or equatorial positions. At high bromotrichloromethane concentrations, the transfer rate is fast and the products formed are mainly from intermediate radical XX_a. At low bromotrichloromethane concentrations, XX_b would be the predominant form, and products would arise from this intermediate. That more XVI is formed in the latter case suggests that equatorial attack is favored over axial attack in the bromine atom transfer step. Such equatorial attack in the six-membered ring system is not unprecedented. Equatorial attack has recently been reported to be faster than the axial attack in some cases,[43a] although addition of $Br\text{-}CCl_3$ to cyclohexane has been described in terms of exclusive axial attack.[43b] Steric hindrance may be the reason for the discrimination between axial and equatorial bromine atom transfer. A study of models for the conversion of XX_b to products suggests that the equatorial position is more open for the incoming atom or group.

Bromoform also added to I in a similar fashion to give a major product (XXI) which was isolated by elution chromatography. The infrared spectrum of this adduct (Fig. 11) includes absorptions at 14.49 and 14.93 μ, indicative of the presence of C-Br and CBr_2. The nmr spectrum (Fig. 12) of XXI consists of a doublet at -5.76 ppm (1H,

J=4Hz, -C<u>H</u>Br$_2$), a sextet at -3.95 ppm (1H, J=9.5, 2.5Hz, -C<u>H</u>Br), and a complex multiplet between -1.0 and -3.00 ppm. The structure XXI is assigned on the basis of the spectroscopic data and considerations similar to those for the 1-bromo-4-trichloromethyl-decalin.



XXI

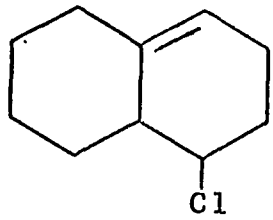
Perhaps it should be pointed out here that the reaction of I with bromoform differs from that with chloroform because the former involves dibromomethyl radical whereas the latter involves trichloromethyl radical. In other words, the C-H bond is broken in the chloroform case while the C-Br bond is broken in the bromoform one. Considering the bond energies of CCl_3-H=95.7 and $CHCl_2$-Cl=72, and CBr_3-H=93 and $CHBr_2$-Br=56 Kcal/mole,[44] one must conclude that the bond dissociation energy difference is not the sole factor which effects the formation of the radical. Other factors such as the stabilities of product radicals may play an important role. For the formation of $\cdot CHCl_2$ and $\cdot CCl_3$ from $CHCl_3$, Kosower and Schwager[45] have estimated stabilization energies for the product radicals relative to methyl radical as: $\cdot CHCl_2$, 10 Kcal/mole; $\cdot CCl_3$, 17 Kcal/mole.

<u>Ionic and Radical Additions</u>

From the foregoing study, it appears that both ionic and radical additions occur with transannular cycloaddition to give substituted

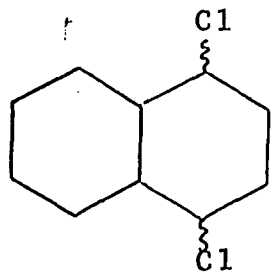
decalins as major products. It is, therefore, desirable to compare these two processes directly by using reagents which can react both ways. Molecular chlorine, iodobenzene dichloride,[24] and bromine azide[23] are reagents reported to add to alkenes by both mechanisms, depending upon the conditions used. Reactions of I with each of these reagents under both conditions gave products resulting from the transannular cycloadditions.

The photoinitiated addition of molecular chlorine to I under a nitrogen atmosphere occurred exothermicly and was complete within 10 minutes. Gas chromatographic analysis of the reaction mixture revealed that there was a peak with a shoulder of longer retention time. This peak and the shoulder were responsible for about 80% of the total area of the reaction mixture chromatogram. The nmr spectrum of the reaction mixture showed very little absorption due to olefinic protons. Distillation of the crude products at reduced pressure gave three distillate fractions. Fraction 1 of the distillate contained one major component which was purified by preparative gas chromatography. The infrared spectrum (Fig. 13) of the adduct included absorption at 3.28 μ, indicative of the presence of C=C-H (C-H stretching). The nmr spectrum (Fig. 14) of this compound consisted of a doublet at -5.52 ppm (1H, C=C-H, J=1.5 Hz), a multiplet at -4.18 ppm (1H, -CHCl), and multiplets between -1.30 and -2.80 ppm (13H, the rest of the protons). The structure of this compound based on the spectral data is assigned as 5-chlorobicyclo-[4.4.0]dec-1-ene (XXII).



XXII

Fractions 2 and 3 were shown by temperature-programmed gas chromatography to consist of two components in about equal amounts. No attempt was made to separate these two components. The infrared spectrum (Fig. 15) of these fractions show no absorptions due to olefinic double bond. The nmr spectrum (Fig. 16) of the mixture consists of multiplets at -4.10 ppm (2H, CHCl), between -1.8 and -2.4 ppm, and at -1.45 ppm. The ratio of the area of the downfield protons (at -4.10 ppm) and the upfield protons (between -1.2 and -2.4 ppm) is 1 : 7 or 2 : 14. These data suggest that the two compounds are isomeric 1,4-dichlorodecalins (Structure XXIII).



XXIII

The addition of molecular chlorine to I in the presence of atmospheric oxygen (ionic conditions) gave similar results as in the case of nitrogen sweep (radical conditions) reaction except that it required a longer reaction time (2 hours). The major products (about 80 area percent) were identified as 1,4-dechlorodecalins (Structure XXIII) by comparing their retention times with the compounds obtained from the

nitrogen-sweep reaction.

Two things are indicated from the reactions of molecular chlorine with I. First, the addition of chlorine to I in the presence of atmospheric oxygen proceeded much slower than the photoinitiated reaction in the absence of oxygen. Therefore, it is reasonable to assume that the reaction involved mainly an ionic process in the former case and a radical chain process in the later one. Second, the absence of a substantial difference in the product distributions between these two processes suggests that the factors which control the initial addition of chlorine atom to I and the product forming step may be the same in both cases. If this is the case, then the isomeric 1,4-dichlorodecalins will have cis stereochemistry at their ring junctures, because ionic additions of reagents to I usually involve transannular cycloadditions to give substituted cis-decalins as products.

The addition of chlorine to I by use of iodobenzene dichloride as halogenating agent has been studied. The reaction in the presence of atmospheric oxygen required 4.5 hours of reaction time, but the reaction in the absence of oxygen occurred spontaneously as the reaction mixture, which was degassed by a freeze-thaw method, warmed to room temperature. Gas chromatographic analyses of the reaction mixtures showed that both reaction mixtures consisted of six components with slightly different distributions. Table III summarizes the results from these two reactions.

TABLE III

Product Distributions from the Reactions of

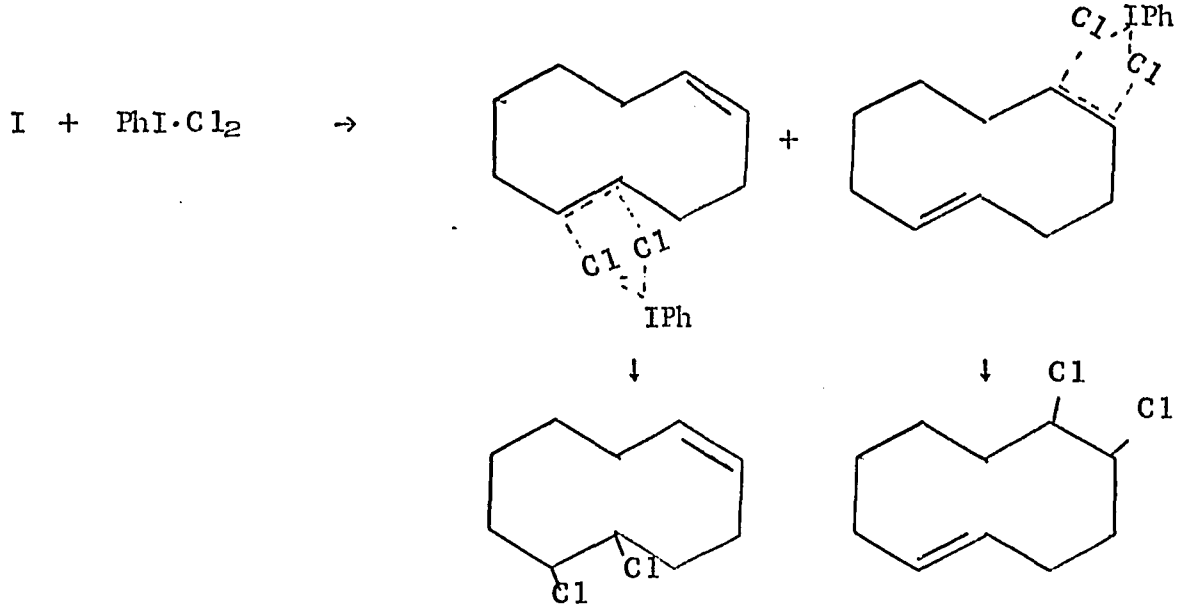
Iodobenzene Dichloride with I

Component	1	2	3	4	5	6
Retention time (min.)	12.0	12.8	14.0	30.2	32.4	34.4
Relative area:						
with oxygen	23	13	13	19	27	5
no oxygen	17	18	17	15	29	4

The component with retention time of 12 minutes was identified as 5-chlorobicyclo[4.4.0]dec-1-ene (XXII) by comparing its retention time with that of the previously identified compound obtained from the addition of molecular chlorine to I in the absence of oxygen. The components with retention times of 30.2 and 32.4 minutes were again identified as 1,4-dichlorodecalin on the basis of gas chromatography.

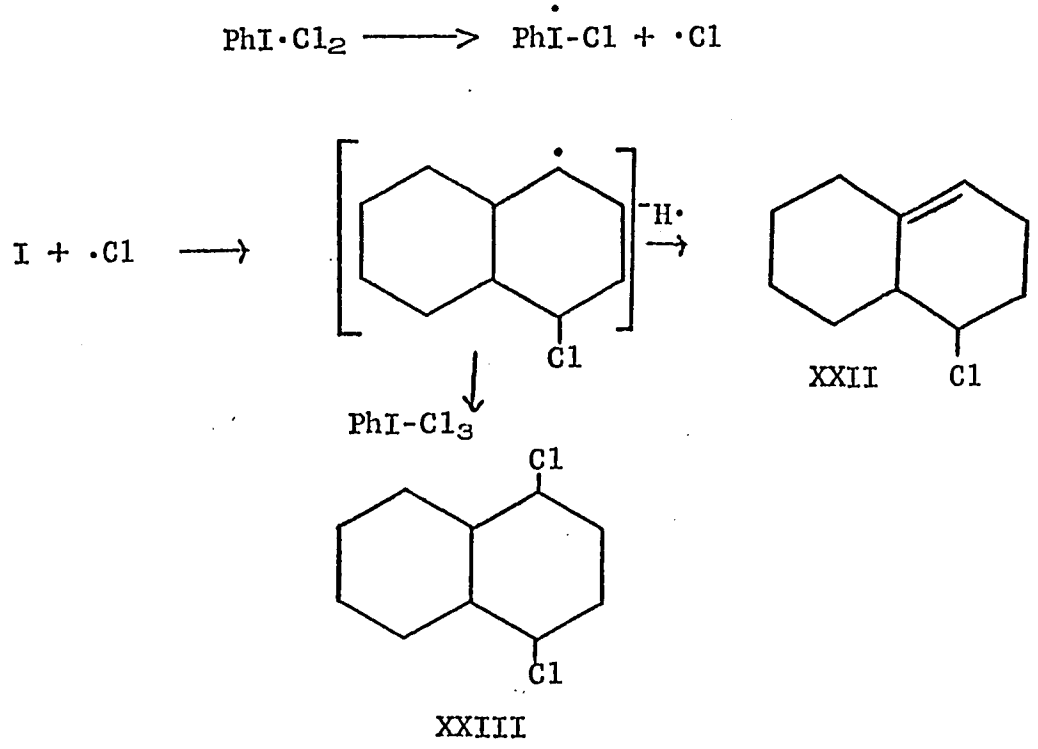
The slow rate of the reaction in the presence of oxygen and the spontaneous, rapid reaction in the absence of oxygen, and the products observed in the addition of iodobenzene dichloride to I are of special interest, because they provide a means of differentiating the possible mechansisms involved in these reactions. The products XXII and XXIII from the reaction of iodobenzene dichloride in the presence of oxygen are those one would expect from an ionic reaction mechanism. The same products observed for the reaction in the absence of oxygen, however, cannot be explained by a molecular addition mechanism. A molecular addition process such as that proposed by Barton and Miller[25] would be

expected to give 1,2-addition products, the 5,6-dichlorocyclodecenes show below.



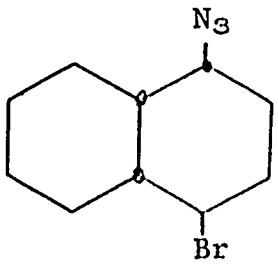
The formation of transannular products from the spontaneous reaction which occurred when iodobenzene dichloride has reacted with I in the absence of oxygen are accommodated by a free radical chain process (Scheme 6).

Scheme 6



XXIII

Ionic addition of bromine azide to I gave an oil, whose infrared spectrum showed strong absorption at 4.75 μ, indicative to an azide functional group. The nmr spectrum of the oil included complex multiplets between -3.25 and -4.65 ppm, in the range of protons germinal to a bromo or azido substituent in the cyclohexane ring system. Although the product has not been obtained in a pure state and the nmr spectrum obtained was not completely analysed, the fact that ionic reactions of reagents with I usually lead to transannular addition products as well as the primary spectral data suggest 1-bromo-4-azidodecalin (XXIV) as the probable product.



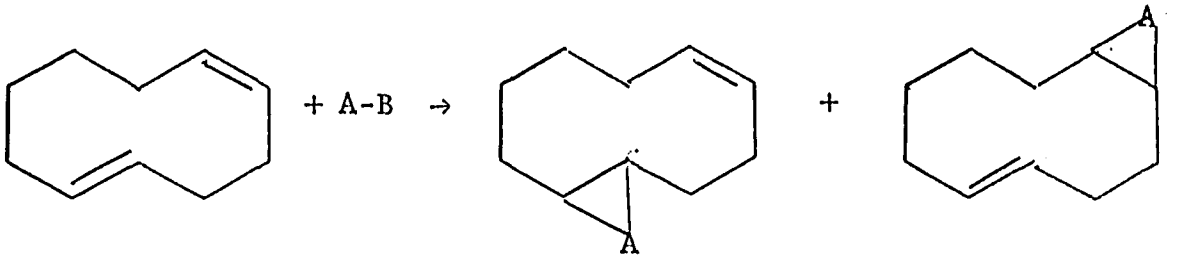
XXIV

The addition of bromine azide to I under radical conditions gave an oily material which also included azide group absorption (4.75 μ) in its infrared spectrum. The nmr spectrum of this oil included some absorptions due to olefinic protons (-5.0 to -6.0 ppm), and, like the spectrum of the ionic reaction product, it had complicated signals between -3.25 and -4.65 ppm. Unfortunately, the limited results do not allow one to have further comparison at the moment between ionic and radical processes, which was the reason for studying these reactions.

Addition of Carbenes to cis,trans-1,5-Cyclodecadiene

Reactions of several carbenes with I all resulted in the formation of bicyclo[8.1.0]undecenes as products (Scheme 7). Like the cis-addition reactions with I[1,2] and with cis,trans,trans-1,5,9-cyclododecatriene,[3,4] these carbene additions occur preferentially at the trans double bond in the diene I (product XXV). Table IV summarizes the results of this study, and the data from the literatures are also included in this table for comparison.

Scheme 7



I

XXV
cis addition to
trans double bond

XXVI
cis addition to
cis double bond

XXV_a and $XXVI_a$, $A=CH_2$
XXV_b and $XXVI_b$, $A=CBr_2$
XXV_c and $XXVI_c$, $A=(CH_3)_2C=C$

TABLE IV

Product Distributions in Reactions Yielding 1,2-Addition

Products with cis,trans-1,5-Cyclodecadiene

Addition Species	Addition Reagent	Addition Products	% Yield	Relative % Addition		Reference
				cis	trans	
$:CH_2$	methylene iodide, Zn-Cu couple	bicyclo[8.1.0]undec-5-enes	60	11	89	This work
$:CH_2$	diazomethane, copper	bicyclo[8.1.0]undec-5-enes	poor	27	73	This work
$:CBr_2$	bromoform, potassium t-butoxide	11,11-dibromobicyclo-[8.1.0]-5-undecenes	70-75 (75)	20-25 (21)	75-80 (79)	This work 46
$C=C(CH_3)_2$	5,5-dimethyl-N-nitrosooxazolidone lithium ethoxyethoxide	11-isopropylidene-bicyclo[8.1.0]-5-undecenes	75	30	70	This work
$:CCl_2$	ethyl trichloroacetate, potassium t-butoxide	11,11-dibromobicyclo-[8.1.0]-5-undecenes	74	25	75	46
O	m-chloroperbenzoic acid	5-epoxycyclodecenes	81.5	10-15	85-95	1,2
2H	diborane	cyclodecenes cyclodecane	70	14	86	1
2H	diimide	cyclodecenes cyclodecane	73	1	99	1
2H	hydrogen, palladium catalyst	cyclodecenes cyclodecane	93	19	81	1

All of the reactions listed in Table IV are considered to be cis-additions. Additions to either the cis or the trans-double bond in the diene I are most conveniently determined by comparing the infrared absorptions at about 10.4 μ and 14.2 μ, which are present in I and correspond to the trans- and cis-double bond absorptions, respectively. Diminished intensity at 10.4 μ may be taken as evidence for addition predominately at the trans-double bond. In this study, however, further documentation and identification were obtained by isolation of the major component, in some cases both components, by preparative gas chromatography. The spectral data of the isolated products were analyzed.

The methylenation of I with methylene iodide and zinc-copper couple has been studied previously.[47] It was noted that the mono-cis-addition to diene I occurred at both the cis- and trans-double bonds, with the addition to the trans double being predominant. This conclusion was supported by the observation that the infrared absorption at 10.4 μ (trans C=C) was reduced in intensity by the reaction. Gas chromatography showed one peak with a shoulder of longer retention time. In order to determine the isomeric product distributions, the reaction was repeated and the reaction mixture was analyzed by temperature programmed gas chromatography to resolve these two isomers. The yield of the monoadducts was about 60%, and ratio of addition to the cis- and trans-double bonds was estimated to be 11 : 89, respectively.

Reaction of I with diazomethane[48] and copper also gave methylenation products. The yield from this reaction was quite low. The selectivity for the cis- and trans-double is not so high as in the

methylenation with methylene iodide and zinc-copper couple. The ratio for addition to cis- trans-double bonds, is 27:73.

Addition of dibromocarbene, generated from bromoform and potassium t-butoxide,[49] gave mono-addition products in 70-75% yield. The ratio of additions to cis- : trans-double bond, was 20-25 : 75-80. The uncertainty of the proportions is due to the fact that decomposition occurred in the column at the temperature of 150°C. The major component of the reaction mixture was isolated by preparative gas chromatography. The infrared spectrum (Fig. 17) of the adduct includes absorptions at 3.28 (m), and 14.25 (s) μ, indicative of the presence of a cis double bond. The nmr spectrum (Fig. 18) consists of multiplets at -5.40, -2.25, -1.65, and -1.15 ppm, and the ratios of the intensities of these signals are 2:8:4:2, respectively. The structure of the compound assigned on the basis of these data is trans-11,11-dibromobicyclo[8.1.0]-cis-undec-5-ene. The minor component is then assumed to be the isomer resulting from addition to the cis-double bond.

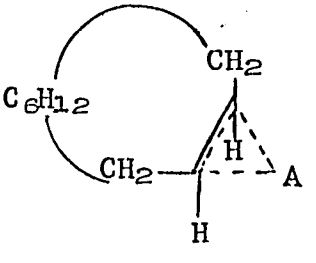
The last cis-addition reagent used for this study was 5,5-dimethyl-N-nitrosooxazolidone with strong base gives the carbene, isopropylidene-methylene, which can be trapped by the use of an olefinic substrate.[50] As with other carbene species, there is concern about whether this one exists as a free carbene or in a complex form. The mechanistic aspects of the addition of such a species, whatever it is, are also of great interest. When I was reacted with 5,5-dimethyl-N-nitrooxazolidone in the presence of a strong base, such as lithium 2-ethoxyethoxide, two major products from the mono-addition of isopropylidenemethylene to I

were formed in 75% yield. The ratio of these two components was estimated to be of 70 : 30, and the predominant component had the shorter retention time. The major component of the reaction mixture was isolated by preparative gas chromatography. The infrared spectrum (Fig. 19) of this adduct includes absorptions at 5.61 μ (D=C), and 14.20 μ (cis C=C). The nmr spectrum (Fig. 20) of this adduct includes a multiplet at -5.40 ppm (2H, CH=CH), a sharp singlet at -1.70 ppm (6H, CH_3), a broad signal at -0.95 ppm (2H, bridgehead protons), and a complex multiplet between -1.4 and -2.5 ppm (12H, the rest of the protons). All these data suggest that this component resulted from the addition of isopropylidenemethylene to the trans double bond in I. Thus the structure assigned is trans-11-isopropylidenebicyclo[8.1.0]-cis-undec-5-ene.

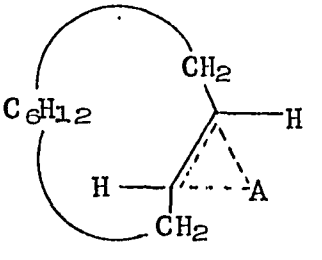
The other minor product was also isolated by preparative gas chromatography. The infrared (Fig. 21) spectrum of this product, differs from that of the major product in that the former has an absorption band at 10.4 μ, which is due to the trans double bond. The nmr spectrum (Fig. 22) of this compound also differs from that of the major product. For the minor component, the downfield signal due to olefinic protons is at -5.55 ppm, the signal at -1.70 ppm appears as two lines rather than a singlet, and an upfield signal appears at -1.25 ppm rather than at -0.95 ppm. The structure of this compound, based on these data, is assigned as cis-11-isopropylidenebicyclo[8.1.0]-trans-undec-5-ene.

From the present study and the data from the literature cited in Table IV, it appears that all the cis addition reagents with various

selectivity add to the trans double bond in preference to the cis double bond in I. What then is the reason for such discrimination? From the introductory section, one realizes that the trans double bond is less stable than the cis double bond in the ten membered ring. This difference might account for such selectivity. When one considers the trans-preference observed in additions to cis,trans,trans-1,5,9-cyclododecatriene, in which a single trans double bond is more stable than a single cis one, one is forced to consider that relative stability is not the major factor in determining the selectivity. A transition state model consideration, however, is useful. As an alkene approaches an addition transition state, substituents on the C-C approach more closely to each other. If the transition state of the concerted, cis addition of reagents to olefins is pictured as follows, it is not hard to see that a higher degree of eclipsing occurs when the cis double bond is attacked by a cis addition reagent than when the attack comes at the trans double bond.



Attack on
cis C=C

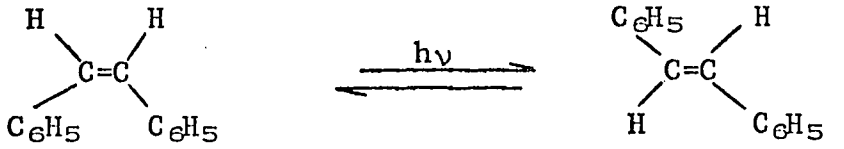


Attack on
trans C=C

Therefore, cis addition to cis double bond is a higher energy process, and cis addition to the trans double bond is more favorable.

Photoisomerization of cis,trans-1,5-Cyclodecadiene

The simplest type of photochemical rearrangement involving olefins is the cis-trans isomerization about a carbon-carbon double bond. This type of photochemical transformation is of theoretical importance and is useful synthetically. In the case of simple monoolefins, it is frequently possible to predict the qualitative cis-trans isomer distribution at the photostationary state, because one can control the factors, such as solvent, energy of the sensitizer, temperature, and concentration, which effect the product distribution.[26] Take the most throughly examined case, the cis-trans isomerization of stilbenes, as an example. At low sensitizer energy or in polar solvent, the mixture is rich in trans isomer; however, if the energy of the sensitizer moves up to about 50 Kcal/mole or if the equilibration is conducted in a less polar solvent, the cis isomer is favored over the trans isomer.[26,51]

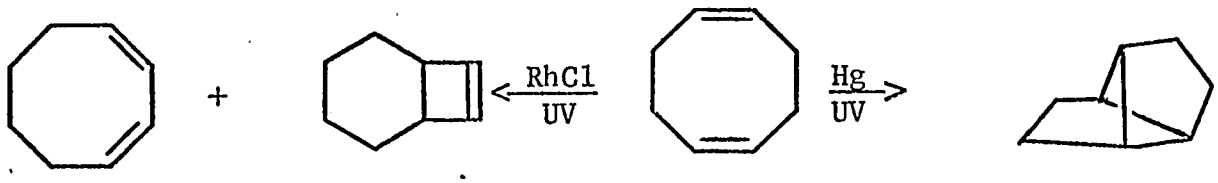


cis-stilbene trans-stilbene

Several photochemical reactions of cyclooctadienes and cyclodecadienes have recently been reported. Correlation of the photochemical behavior of these dienes is complicated by the occurrence of an intramolecular cycloaddition and C=C positional isomerization, in addition

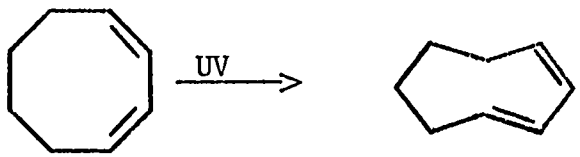
to the commonly observed cis-trans isomerization. The following examples from the current literature support this statement.

The mercury-sensitized or copper(I) chloride-catalyzed photoisomerization of cis,cis-1,5-cyclooctadiene (XXVII) yields a tricyclooctane (XXVIII) as product,[52] whereas the product obtained with rhodium(I) chloride catalysis gave cis,cis-1,3-cyclooctadiene (XXIX) and bicyclo[4.2.0]oct-7-ene (XXX).[53]

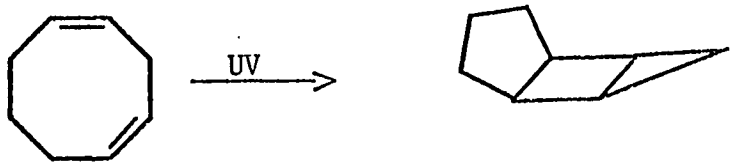


XXIX XXX XXVII XXVIII

While cis,cis-1,3-cyclooctadiene (XXIX) undergoes photosensitized isomerization to cis,trans-1,3-cyclooctadiene (XXXI),[54] the cis,cis-1,4-cyclooctadiene-(XXXII) gives an internal photocycloaddition product, cis-syn-cis-tricyclo[3.3.0.$0^{2,4}$]octane (XXXIII)[55].

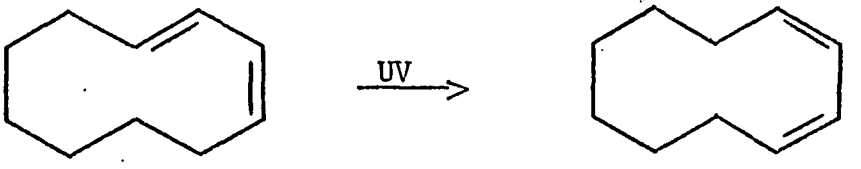


XXIX XXXI

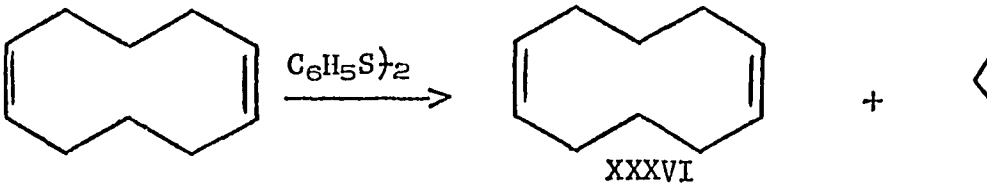


XXXII XXXIII

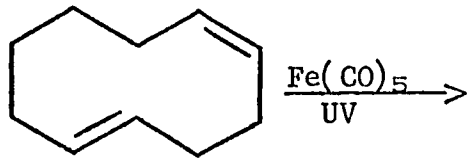
Photochemical rearrangements in the cyclodecadiene series are as ununiform as in the cyclooctadiene series. Irradiation of cis,trans-1,3-cyclodecadiene (XXXIV) gave cis,cis-1,3-cyclodecadiene (XXXV) quantitatively;[56] irradiation of cis,cis-1,6-cyclodecadiene (XXXVI) in the presence of diphenyl disulfide resulted in an equilibrium mixture of cis,cis- and cis,trans-1,6-cyclodecadienes (XXXVI and XXXVII);[57] and iron pentacarbonyl-catalyzed photoisomerization of cis,trans-1,5-cyclodecadiene(I) resulted in the formation of cis,cis- and trans,trans-1,6-cyclodecadienes (XXXVI and XXXVIII).,[17] products of C=C migration. In addition to these hydrocarbon isomerizations, the photoisomerization of cis,cis-cyclodeca-3,8-diene-1,6-dione (XXXIX) has been reported to occur with both cis,trans-isomerization (XL) and intramolecular cycloaddition (XLI or XLII).[58,59]



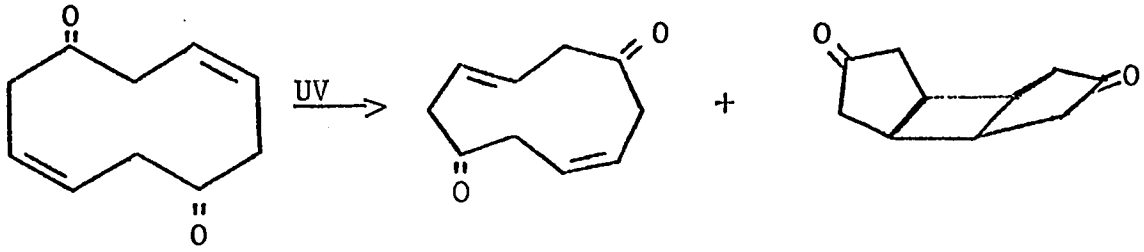
XXXIV XXXV Ref. 56



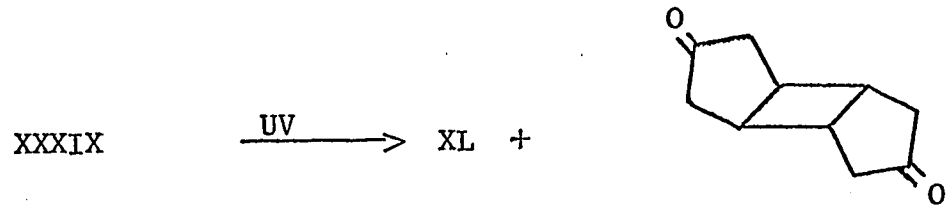
XXXVI XXXVII Ref. 57



I XXXVI + XXXVIII Ref. 17



XXXIX XL + XLI Ref. 58



Ref. 59

XLII

Two conclusions which motivate this isomerization study are: 1) Some but not all radical additions to cis,cis-1,5-cyclooctadiene yield substituted bicyclo[3.3.0]octanes as products;[22, 60] these processes involve transannular C-C bond formation resembling that in the photoisomerization of the same diene. 2) As the study of radical and ionic addition reactions with I discloses, the tendency for such transannular C-C bond formation is apparently much greater with cis,trans-1,5-cyclodecadiene than with cis,cis-1,5-cyclooctadiene.

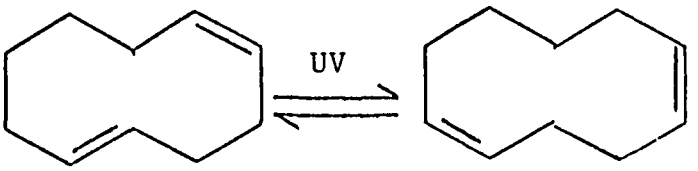
Irradiation of a solution of I in ethyl ether containing small amounts of copper(I) chloride with sixteen 2537 Å lamps surrounding the reaction flask (Rayonet Photochemical Reactor) produced a mixture of I and cis,cis-1,5-cyclodecadiene (XLIII) (Scheme 8). After 120 hours of irradiation, the relative amounts of I and XLIII did not change further, and the ratio of I and XLIII in the reaction mixture was estimated by gas chromatography to be 1 : 4. Prolonged irradiation led to the conversion of the dienes to high-boiling, yet unidentified materials, but gas chromatographic analysis of the reaction mixture at short reaction time revealed XLIII as the only product from I. Similar results were also obtained from the xylene-sensitized photoisomerization of I. Table V summarizes the time-dependent product distributions in the xylene-sensitized isomerizations.

TABLE V

Product Distributions in Xylene-sensitized Photoisomerization of cis,trans-1,5-Cyclodecadiene

Reaction Time (hours)	I	XLIII
20	73	79
46	46	54
89.7	28.2	71.8
100	21	79

Scheme 8



I XLIII

I and XLIII can be separated by fractional distillation; however, it is more convenient to separate these two isomers by preparative gas chromatography under the conditions described in the experimental section. Ths isomeric dienes are readily distinguished by their infrared and nmr spectra. The infrared spectrum (Fig. 23) of XLIII includes absorptions at 13.52 and 14.0 μ (cis C=C) but none at 10.02 and 10.43 μ (trans C=C), which are in the spectrum of I. The nmr spectrum (Fig. 24) of XLIII is consistent only with the 1,5-diene assignment; it consists of four multiplets of equal area centered at -5.38 (C=CH), -2.34 (C=C-CH, -CH, -C=C), -2.16 (C=C-CH_2-CH_2-CH_2-CH_2-C=C), and -1.50 ppm (C=C-CH_2-CH_2-CH_2-CH_2-C=C). A 1,6-cyclodecadiene would give three nmr absorptions for C=CH, C=CCH, and $CH_2CH_2CH_2$, with relative intensities of 2 : 4 : 2, respectively. A 1,4-cyclodecadiene would give four absorptions with relative intensities of 1:1:2:3. That these absorptions correspond to the protons indicated was confirmed by spin decoupling experiments to yield the expected simplified spectra (Fig. 25). The mass spectrum of XLIII included a peak at m/e 136, as expected for its parent ion, and intense peaks at m/e 79, 67, 54, 53, 41, 29, 28, and 27.

In spite of the driving forces which tend to form transannular cyclization products in the ionic and radical addition reactions with I, no "cross" or "straight" cycloaddition was detected in this photoisomerization study. Instead, the photoisomerization of I promoted by copper(I) chloride or xylene is the more commonplace cis,trans-isomerization. From Table 5, it can be seen that the reaction mixture is rich in cis,cis-isomer at the photostationary state, which was more rapidly established when XLIII was the starting diene with xylene as sensitizer. This cis,trans-isomerization provides an easy route to the previously unreported cis,cis-1,5-cyclodecadiene (XLIII), which would be hard to synthesize by other methods.

Relative Reactivities of cis,trans- and cis,cis-1,5-Cyclodecadienes

In order to obtain some information about the relative reactivities of the geometrical isomers obtained from the photoisomerization study, I and XLIII were compared by thermal rearrangements and by addition reactions with trifluoroacetic acid.

Both cyclic dienes undergo thermal rearrangement to cis-1,2-divinylcyclohexane (XLIV), but, in contrast to the photoconversion of I and XLIII, the cis,cis-diene (XLIII) rearranges thermally at a much slower rate than the cis,trans-diene(I) does. The conversion of I to XLIV was more than 99% complete after 44.5 hours of heating at 125°C, but only 3% of XLIII was converted to XLIV by the same heating (see Table VI).

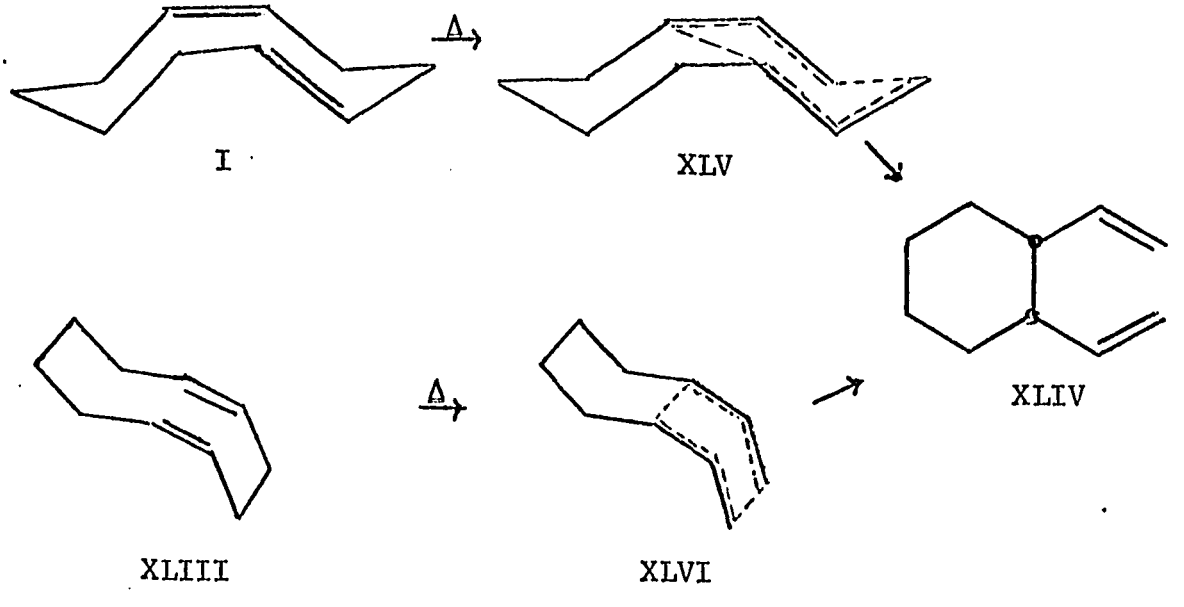
TABLE VI

Product Distributions of the Thermal Rearrangent of I and XLIII to XLIV

Heating Time	% Conversion of (I) to (XLIV)	% Conversion of (XLIII) to (XLIV)
1	16.6	-
6	69	-
$20\frac{1}{2}$	97	-
$44\frac{1}{2}$	99%	3%

The thermal rearrangements of I and XLIII to XLIV are in accord with the well-established orbital symmetry theory of Hoffmann and Woodward.[61] According to these authors, the well-known Cope rearrangements are sigmatropic changes, of order (3,3), which occur with retention of configurations at the shifting sites. (Scheme 9).

Scheme 9



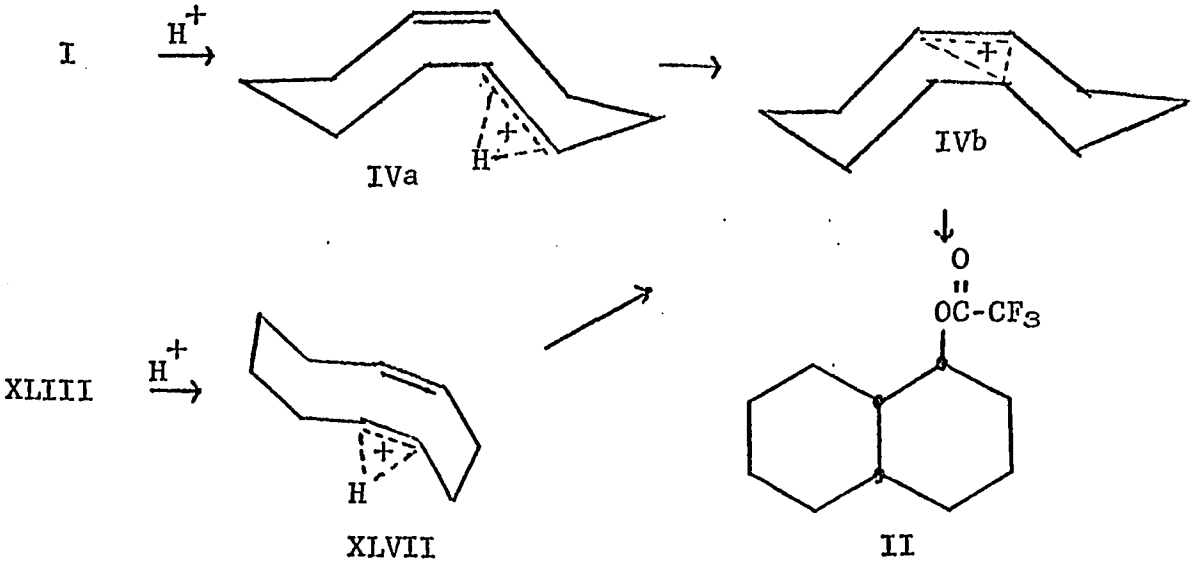
Since the Cope rearrangement is believed to involve a concerted, six-membered transition state mechanism,[62] the difference in the rates of isomerization of the two cyclic dienes is easily explained by the considerations of models. Models suggest that the detailed geometries for the rearrangement of I and of XLIII to XLIV are quite different. In the conversion of I to XLIV, the transition state probably resembles the relatively stable pseudo chair-chair conformation (XLV). In the conversion of XLIII to XLIV, however, the transition state probably resembles the pseudo boat-boat conformation (XLVI), which is one of the least favorable conformations; therefore, this process has higher energy requirements. Thus, the rate difference reflects the detailed geometry of the reacting system in the transition state; it does not necessarily reflect the ground state energy difference between I and XLIII.

Like I, XLIII reacts rapidly with trifluoroacetic acid without external heating to form cis-1-trifluoroacetoxy-cis-decalin (II). A qualitative estimate of the relative rates of the dienes was made by noting the times for disappearance of olefinic proton absorptions in the nmr spectra of the dienes in trifluoroacetic acid solutions. After 6 minutes, the reaction of I appeared to be about 90% complete, and that of XLIII to be about 50% complete.

That both I and XLIII react with trifluoroacetic acid to give the same product implies that a common intermediate may be involved in the addition processes. The difference in rates is, again, most easily explained by the consideration of models. Models suggest that I is sterically more favorable than XLIII for orbital overlap (involving

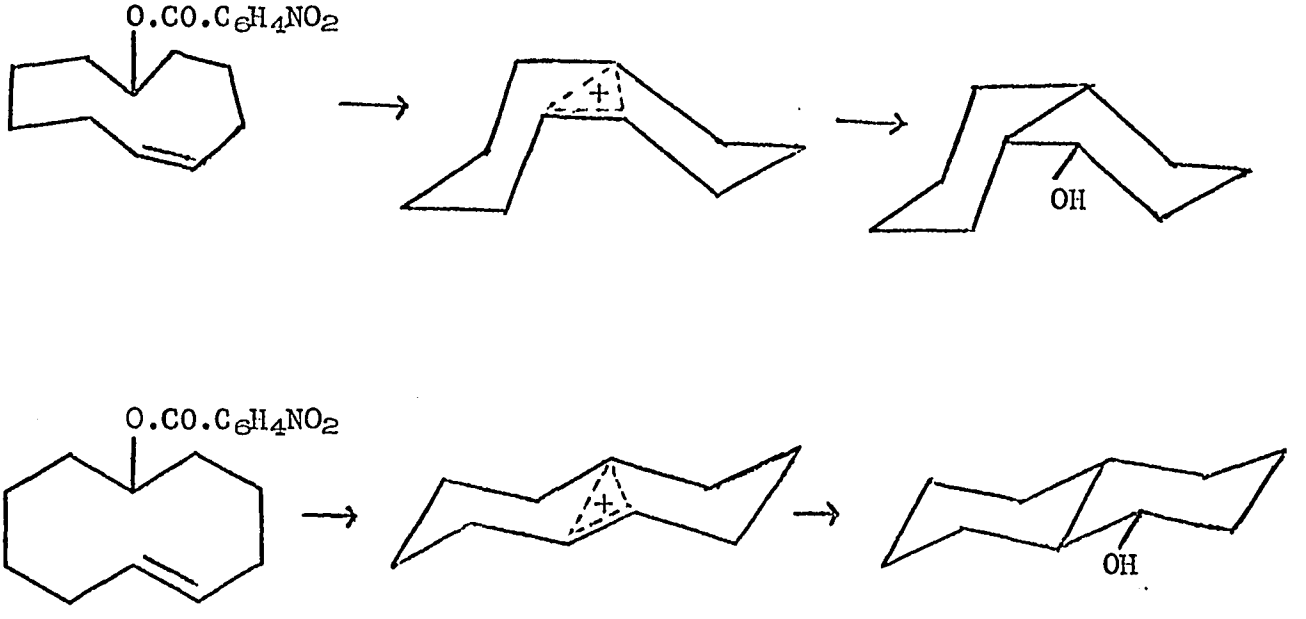
the π-bonds at positions C-1 and C-6) to form a new σ C-C bond. They also suggest that the detailed geometries for initial protonated species from I and XLIII, leading to the common intermediate, are quite different as in the case of thermal rearrangement. In the case of I, the protonation presumably occurs at the trans-double bond and leads to the more energetically favorable pseudo chair-chair conformation (IV_a) in the formation of the common cationic intermediate (IV_b). In the case of XLIII, however, one always encounters the energetically unfavorable conformation, the pseudo boat-boat form XLVII on the way to the common cationic intermediate. Therefore, the energy barrier separating XLIII and XLVII is probably higher than that separating I and IVb, and I reacts faster than XLIII. The following scheme 10 outlines the possible mechanisms for the formation of the common product.

Scheme 10



The initial protonation in I is postulated to occur at the trans double bond in keeping with the fact that ionic reactions with I frequently occur stereoselectively. The bridged intermediate is not assured, but it has been postulated in the solvolysis of cis- and trans-

5-cyclodecen-1-yl-p-nitrobenzoates to explain both the faster rate of these unsaturated esters compared to that of the corresponding saturated ester, and the stereospecific formation of products, cis,cis and trans,trans-decalols, respectively.[63]



CHAPTER III

EXPERIMENTAL

All boiling points and melting points are uncorrected. Gas chromatographic analyses were performed on a Beckman GC-5 or a Packard 700 instrument equipped with 1/8 in. columns packed with Carbowax 20M (10 ft), silicone SE-30 (6 ft), or tricresyl phosphate (12 ft) on 60-80 mesh solid support. Preparative gas chromatography was carried out on an Aerograph Autoprep Model A-700 instrument. Infrared spectra were obtained with a Beckman IR-10 spectrometer. Nmr spectra of $DCCl_3$ or CCl_4 solutions were recorded on Varian Associates HA-60 and HA-100 instruments with the assistance of William Wegner; all chemical shifts are given relative to internal tetramethylsilane(TMS) reference (minus indicates downfield). Mass spectra were obtained on a Varian Associates M66 instrument by Cheryl White. Microanalyses were performed by Ralph Seab in these laboratories.

A. Preparation of cis,trans-1,5-Cyclodecadiene

cis,trans-1,5-Cyclodecadiene was prepared by cyclooligomerization of 1,3-butadiene and ethylene with nickel-bis-1,5-cyclooctadiene catalyst.[18] The detailed steps for the synthesis of the catalyst and the diene are described below. All of the following reactions and workup procedures were performed in nitrogen atmospheres.

1. Ethoxydibutylaluminum

Because of the availability in these laboratories of the butylaluminum reagent, ethoxydibutylaluminum was used as reducing agent instead of ethoxydiethylaluminum[18,64] for the preparation of the needed catalyst. Ethoxydibutylaluminum was prepared by the reaction of

equimolar amounts of tributylaluminum and absolute ethanol in benzene solution. During a one hour period, 18.2 g (0.39 mole) of ethanol was added to a solution of 78.2 g (0.39 mole) of tributylaluminum in 200 ml of benzene at room temperature. The mixture was stirred for another eight hours. The resulting product was then concentrated to about 150 ml under vacuum and used without further purification.

2. Nickel-bis-1,5-Cyclooctadiene[64]

Nickel acetylacetonate (40 g, 0.4 mole) was dissolved in 300 ml of air-free benzene under nitrogen gas, and 40 g of freshly-distilled cis,-cis-1,5-cyclooctadiene was added. The solution was cooled to 0°C, and the ethoxydibutylaluminum in benzene solution prepared above was added dropwise during one hour. The resulting mixture was then stirred for 15 hours at 0°C. The precipitated yellow crystals was filtered with suction and washed several times with cold benzene; 48 g of nickel-bis-1,5-cyclooctadiene was obtained. As the compound is very sensitive to air, no physical properties were measured. It was stored in a nitrogen atmosphere before use.

3. Preparation of cis,trans-1,5-Cyclodecadiene

The nickel-bis-cyclooctadiene obtained above was placed in a nitrogen flushed, compressed gas cylinder from which the valve had been removed. About 1000 g of butadiene was charged into the cylinder, the valve was replaced, and ethylene was added until the total pressure in the reaction cylinder reached 150 psi. The sealed cylinder was then allowed to stand at room temperature for three weeks. Samples were taken by venting off some of the reaction mixture from time to time,

and the progress of the cyclooligomerization was followed by gas chromatography. At the end of the reaction time, the excess ethylene was released, and the liquid contents of the cylinder were separated from the catalyst by filtration. The filtrate weighed 1100 grams. Gas chromatography revealed that the mixture consisted of about 40-45% cis,trans-1,5-cyclodecadiene; 47-50% isomeric cyclododecatrienes; 4-9% cyclooctadiene, 1,2-divinylcyclohexane, and 4-vinylcyclohexene combined; and 1% other unidentified products. Distillation of the mixture under vacuum (0.7 mm Hg) gave four fractions [(1) 24-26°C, 80 g; (2) 26-36°C, 400 g; (3) 36-51°C, 130 g; (4) 51-55°C, 460 g.] plus undistilled, viscous residue. Fraction 1 contained three components which were identified as 4-vinyl-1-cyclohexene, cis,cis-1,5-cyclooctadiene, and cis-1,2-divinylcyclohexane by comparing their gas chromatography retention time with the known compounds. Fraction 2 and 3 contained mainly the desired product, cis,trans-1,5-cyclodecadiene, with some cyclooctadiene and cyclododecatriene. Fraction 4 contained three isomeric cyclododecatrienes. Redistillation of fractions 2 and 3 at 51-53°C (4.8 mm Hg) yielded 400 g of 98% pure cis,trans-1,5-cyclodecadiene (I). The compound was characterized and compared with a known sample. The infrared spectrum included strong absorption at 10.29 (trans C=C), and 14.24 (cis C=C) μ. The nmr spectrum was identical with that of an authentic sample.[65]

B. Ionic Additions of Reagents to cis,trans-1,5-Cyclodecadiene

1. Addition of Trifluoroacetic Acid

To stirred trifluoroacetic acid (15 ml) in a flask was added 2.72 g (20 mmoles) of I drop by drop in 30 seconds. The temperature of the reaction mixture rose to 58°C in one minute and began to drop a few minutes later. The solution was then allowed to stir for 30 minutes. The color of the mixture changed gradually from light yellow to brown. At the end of the reaction time, the mixture was poured into 100 ml of ice water and was extracted several times with ethyl ether. The combined ether solution was washed first with 10% sodium bicarbonate solution and then with water. The separated ether layer was dried over calcium chloride, and the solvent was removed under reduced pressure to yield 4.8 g of crude product. On distillation, 4 g (80%) of pure compound II was obtained (b.p. 99-100.5°C/9 mm Hg). The infrared spectrum (Fig. 1) included absorptions at 3.38 (s), 3.48 (s), 5.57 (s), 6.73 (w), 6.81 (m), 7.10 (m), 7.27 (m), 8.10 (s), 8.51 (s), 9.49 (w), 10.05 (m), 10.20 (m), 10.70 (m), 11.17 (w), 11.38 (w), 12.66 (m), and 13.42 (m) μ.* The nmr spectrum (Fig. 2) of the compound II consisted of a multiplet at -5.0 ppm ($CHOCOCF_3$, 1H), and a broad multiplet between -1.0 and -2.0 ppm (the rest of the ring protons, 16H).

Identification of II was accomplished by hydrolyzing 5 g of II with 15 ml of 2 M NaOH solution to yield the known crystalline compound in quantitative yield. Recrystallization from pentane yielded 2.7 g (93%) of cis,cis-1-decalol: (m.p. 90-91°C). The infrared and nmr spectra

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*In descriptions of infrared spectra in this Dissertation, s, m, and w designate strong, medium, and weak absorption, respectively.

were identical with those of an authentic sample of cis,cis-1-decalol (lit. m.p. 93°).[27,28]

2. Addition of Mercuric Azide[33]

Sodium azide (5.85 g, 0.09 mole) was added slowly to a stirred solution of mercuric acetate (9.24 g, 0.03 mole) in 50 ml of 50% aqueous tetrahydrofuran. After 15 minutes of stirring at room temperature, the original yellow color due to the complexation of mercuric acetate with the solvent disappeared. The diene I (4.0 g, 0.03 mole) was then added to the resulting solution and allowed to react at room temperature for two hours. The two phase mixture was diluted with 20 ml of 15% aqueous potassium hydroxide and treated with a solution of sodium borohydride (0.5 g) in 20 ml of 15% potassium hydroxide solution. After the mixture had been stirred for thirty minutes, free mercury deposited at the bottom of the reaction flask. The two-phase solution was extracted three times with ethyl ether. The combined ether solution was dried over magnesium sulfate, and the ether was removed under reduced pressure, yielding 5.0 g of crude product.

The crude product (4.0 g) was chromatographed on Merck alumina (150 g, acid-washed). It was eluted first with 300 ml of petroleum ether, then with 300 ml of petroleum ether-ether mixtures (3:1, 1:1, and 1:3), and finally with 100 ml of methanol. Thirty-four 30 ml fractions were collected. The solvents were evaporated at room temperature, and the residues were examined by infrared and nmr spectra.

Reaction	Residue
1-3	none
4	<0.1 g, colorless liquid
5	<0.1 g, colorless liquid
6-10	0.6 g, colorless liquid
11-15	none
16-19	1.2 g, colorless liquid
10-24	none
25-28	<0.1 g, yellow oil
29-34	1.8 g, slight yellow crystals

Fraction 4 was identified as the unreacted I. Fraction 5 contained I and the reaction product which was also present in fractions 6-10. The colorless liquid from fractions 6-10 was identified as cis-1-azido-cis-decalin (V, 0.6 g, 11%). The infrared spectrum of V (Fig. 3) has absorption at 4.75 μ, characteristic of an azido group. The nmr spectrum of V (Fig. 4) consists of a multiplet at -3.45 ppm (1H, $C\underline{H}N_3$), and a broad multiplet between -1.0 and 2.1 ppm (16H, cis-decalin framework). Further verification of the structure and stereochemistry of V was achieved by hydrogenation of this adduct to the corresponding amine.

A sample of the azide (0.3 g) obtained above was dissolved in 50 ml of absolute ethanol and was hydrogenated at 45 psi hydrogen pressure with platinum oxide (0.05 g) catalyst at room temperature for four hours.[35] At the end of the hydrogenation, the catalyst was separated by filtration, and, on removal of the solvent, a viscous oil (0.2 g)

was obtained. The crude amine thus obtained was converted to the benzamide derivative by treating the amine (0.2 g) with 1 ml of benzoyl chloride in the presence of three drops of pyridine. The yellowish crystalline compound was collected by filtration and washed with water. The crude benzamide (0.2 g) melted at 202-204°C. Recrystallization from acetone yielded 0.15 g of pure N-(cis,cis-decahydro-1-naphthyl)acetamide, m.p. 205-206°C (lit. 206°).[38] Its infrared and nmr spectra were identical with those of the benzamide obtained from the reaction of I with benzonitrile.

The structure of the colorless liquid from fractions 16-19 has not been established. The infrared spectrum of the adduct includes strong absorption at 4.75 μ indicative of the presence of azido group. There is no absorption attributable to the hydroxyl group or to C-C unsaturation. The nmr spectrum of this adduct consists of multiplets at -3.36 ppm, and at -1.0 to -2.2 ppm. The ratio of these two areas is 1:4. This information suggests that the adduct is an alkyl azide.

The crystalline material from fractions 29-34 was identified as cis,cis-1-decalol (1.8 g, 39%) by comparing its infrared and nmr spectra with an authentic sample. The recrystallized compound melted at 90-91° (lit. 93°).[27,28]

3. Addition of Acetonitrile

To a solution of I (2.72 g, 0.02 mole) and acetonitrile (10 ml) was added 2 ml of concentrated sulfuric acid. The mixture was stirred at room temperature overnight. At the end of that time, the mixture was poured into 20 ml of ice water, and the excess acetonitrile was removed on a rotary evaporator under reduced pressure. The aqueous

solution was extracted four times with chloroform, and the combined chloroform extract was washed with water and then dried over magnesium sulfate. After removal of the chloroform, a white crystalline product (2.5 g) was obtained. The adduct, purified by recrystallization from acetone, melted at 177-179°C; after sublimation, the m.p. increased to 178.6°-180°C. The nmr spectrum of this adduct consists of a broad absorption centered at -5.83 ppm (1H, -NH-C-CH_3), a multiplet at -3.90 ppm (1H, CH-NH-), a singlet at -1.96 ppm (3H, -NHC-CH_3), and a multiplet between -1.0 and -2.0 ppm (the rest of the protons). Its infrared spectrum consisted of absorptions at 2.7-3.18 (broad), 3.06 (s), 3.23 (m), 3.42 (s), 3.48 (s), 6.08 (s), 6.41 (s), 6.85 (m), 6.94 (s), 7.25 (s), 7.36 (w), 7.62 (m), 7.69 (m), 7.81 (w), 8.25 (w), 9.0 (m), 9.8 (w), 10.31 (w), 11.70 (w), and 13.25 (m) μ. These data are consistent with the structure, N-(cis,cis-decahydro-1-naphthyl)-acetamide (lit. m.p. 181°).[27] The yield was 64%.

Anal. Calcd. for $C_{11}H_{21}NO$: C, 73.5; H, 11.2. Found: C, 73.3; H, 10.7.

4. Addition of Benzonitrile

To a solution of I (1.36 g, 0.01 mole) in benzonitrile (10 ml) was added 1.5 ml of concentrated sulfuric acid. The mixture was allowed to stand overnight, was poured into 20 ml ice water, and was extracted three times with chloroform. The combined chloroform extract was washed with water and was dried over magnesium sulfate. After the solvent and the unreacted benzonitrile were distilled off under

reduced pressure, 1.5 g of slightly yellow solid material was obtained. Recrystallization of this crude product from acetone yielded 1.2 g of white crystals, m.p. 205-206°C. The nmr spectrum of this adduct consists of multiplets at -7.60 to -7.86 ppm (5H, aromatic protons), -6.08 ppm (1H, NH-C(=O)-C_6H_5), -4.16 ppm (1H, CH-NH-C(=O)-C_6H_5, and -1.0 to -2.2 ppm (16H, the rest of the protons). Its infrared spectrum consists ob absorptions at 2.70-3.18 (broad), 2.99 (s), 3.06 (s), 3.40 (s), 6.12 (s), 6.21 (m), 6.32 (s), 6.50 (s), 6.70 (m), 6.81 (m), 6.90 (m), 7.48 (m), 7.53 (s), 7.76 (m), 7.91 (w), 8.24 (w), 8.62 (w), 9.16 (w), 9.30 (w), 9.71 (w), 11.77 (w), 12.45 (w), 13.89 (w), 14.32 (s), and 14.82 (w) μ. These data are consistent with the structure, N-(cis,cis-decahydro-1-naphthyl)-benzamide.[38] The yield was 58%.

Anal. Calcd. for $C_{17}H_{23}NO$: C, 79.3; H, 9.0; N, 5.45. Found: C, 79.2; H, 9.1; N, 5.4.

C. Radical Additions of Reagents to cis,trans-1,5-Cyclodecadiene

1. Radical Addition of Chloroform

A solution of I (10 g, 73.6 mmoles) in chloroform (35 g) under a nitrogen atmosphere was irradiated at room temperature for 90 hours with sixteen 2537 Å lamps surrounding the quartz reaction flask. After removal of the excess chloroform, the reaction mixture was shown by gas chromatography (10 ft x 1/8 in. Carbowax 20 M column, 160°) to consist of one major product (66 area %). Three components (18%) with shorter retention time and some high boiling, longer retention time materials (12%) were also present as minor products. Distillation of this mixture under reduced pressure (0.6 mm Hg) gave four fractions

[(1) 25-56°C, 0.7 g; (2) 56-59°C, 1.6 g; (3) 59-90°C, 0.4 g; (4) 90-92.5°C, 6.5 g] and 5 g of undistilled viscous residue. Fractions 1 and 2 contained mainly unreacted diene. Fraction 3 contained three components which showed strong absorptions at 3.31, 6.06, and 13.0 μ in its infrared spectrum; its nmr spectrum also included absorptions in the olefinic region and a multiplet at -2.70 ppm. Fraction 4 contained the major product in about 90% purity. An analytical sample for this adduct was obtained by preparative gas chromatography. The infrared spectrum of the adduct (Fig. 5) includes strong absorptions at 12.8-13.0 μ, indicative of the presence of a trichloromethyl group, and no absorption at wavelength lower than 3.4 μ, attributable to C=C-H stretching vibrations. Its nmr spectrum (Fig. 6) consists of a multiplet (1H, $CHCCl_3$) centered at -2.70 ppm and a complex multiplet between -1.0 ppm and -2.5 ppm (17H, the rest of the protons). The compound gave negative tests for C=C with aqueous potassium permanganate and with bromine in carbon tetrachloride solution. These data suggest that the compound is 1-(trichloromethyl)-decalin.

Anal. Calcd. for $C_{11}H_{17}Cl_3$: C, 52.1; H, 6.7. Found: C, 52.1; H, 7.1.

A sample of the major adduct (2.5 g, 0.01 mole) was allowed to react with an excess of potassium hydroxide (1.5 g) in a mixed solvent composed of 10 ml of dimethyl sulfoxide, 5 ml of methanol, and 2 ml of water at reflux temperature for 5 hours. At the end of the reaction time, the mixture was poured into ice water and extracted three times with 20 ml of ethyl ether. The combined ether extract was dried over anhydrous magnesium sulfate. On removal of the solvent, 2 g of the

starting compound was recovered. The aqueous solution was acidified with hydrochloric acid and then extracted with three 20 ml portion of chloroform. The combined chloroform solution was washed with saturated brine solution. After the extract had been dried over anhydrous magnesium sulfate, the solvent was removed to give 0.2 g of viscous oil. The infrared spectrum of the oil included absorption at 5.87 μ, indicative of the COOH functional group. The nmr spectrum of the oil consisted of a broad signal at 11.8 ppm (1H, -COOH), a multiplet at -2.28 ppm (1H, -CHCOOH), and a multiplet between -1.0 and -2.0 ppm (16H, the rest of the ring protons). These data suggest cis,cis-1-decahydronaphthoic acid as the possible product. Attempts to isolate the acid in the crystalline state were not successful.

2. Radical Additions of Bromotrichloromethane

a. In Excess Bromotrichloromethane

A solution of 10 g (73.6 mmoles) of I and 80 g (40.4 mmoles) of bromotrichloromethane under a nitrogen atmosphere in a quartz flask was irradiated for one hour with sixteen 3500 Å lamps surrounding the flask. The nmr spectrum of the reaction mixture was no longer characterized by signals due to I. The nmr spectrum and gas chromatographic analysis showed that a small amount of chloroform had formed in the reaction mixture. Distillation of the excess bromotrichloromethane under reduced pressure (0.7 mm) at room temperature (25°C) yielded 25 g of crude products. The nmr spectrum of the crude products consists of two sets of sextet signals centered at -4.46 and -3.92 ppm, absorptions in the olefinic region, and absorptions between -1.0 and -2.8 ppm. Distillation of this reaction mixture gave four fractions [(1) 25-130°C, 2 g;

(2) 130-152°C, 2 g; (3) 152-153°C, 7 g; (4) 153-156°C, 10 g] and 3.8 g of undistilled, very viscous material. Fraction 1 contained 3 components, two of which had the same retention times as the minor products obtained from the addition of chloroform to I. Upon cooling to room temperature, fractions 3 and 4 solidified to give slight yellow crystals. Recrystallization of this solid from pentane yielded 15 g of the major adduct(XVI), m.p. 63-65°C. After several recrystallizations from pentane, colorless crystals were obtained, and the melting point increased to 67-69°C. The infrared spectrum of XVI (fig. 7) consists of strong absorption at 12.8 to 13.5 μ, indicative of a CCl_3 group. The nmr spectrum of XVI (Fig. 8) includes a sextet centered at -3.92 ppm (1H, CHBr), a multiplet centered at -2.65 ppm (1H, $CHCCl_3$), and a complex multiplet between -1.0 and -2.5 ppm (16H, the rest of the ring protons). The compound (XVI) was identified as 1-bromo-4-trichloromethyl-cis-decalin.

Anal. Calcd. for $C_{11}H_{16}BrCl_3$: C, 39.5; H, 4.8. Found: C, 39.7; H, 5.0.

Since it was noted that the nmr spectrum of the above reaction mixture included also a sextet signal at -4.46 ppm attributable to an equatorial proton geminal to bromine atom in a cyclohexane ring system, it is desirable to isolate the possible isomer. Unfortunately, many attempts to separate the compound failed. However, elution chromatography of the reaction mixture using florisil or alumina (Merck, acid-washed) as absorbent and pentane as solvent did give some additional information which was not obtained in the fractional distillation. A

crude product (5 g) from the reaction was chromatographed on alumina (150 g, acid-washed) with pentane as eluent. For each fraction, about 30 ml liquid was collected. In the earlier fractions (4-6) of elution chromatography, two components (0.8 g) which were present in the reaction mixture as minor products were obtained. These two compounds had absorptions attributable to the presence of a carbon-carbon double bond and a trichloromethyl group in their nmr and infrared spectra. Although the structures of the two components were not established, gas chromatographic analyses showed that these two compounds had the same retention times as those minor products (XIII, XIV) obtained from the addition of chloroform to I. The solute (1.8 g) in the middle fractions (10-16) was mainly the crystallized product, XVI. In the later fractions (25-28), one component (0.2 g) which was not isolated by distillation was obtained. The nmr spectrum (Fig. 10) of this last component included broad multiplets at -5.33 to 5.75 ppm, -4.00 to -4.40 ppm, and -1.5 to -3.0 ppm, with relative areas of 1 : 1 : 6, respectively. The infrared spectrum (Fig. 9) of this component included absorptions at 14.0 μ (cis-alkene) and 12.8 μ (CCl_3). None of the fractions collected by elution chromatography gave an nmr spectrum which included a signal at -4.46 ppm, although the original mixture did so.

When the original reaction mixture (3.35 g) was treated with half an equivalent of potassium hydroxide (0.28 g) in a mixed solvent composed of 3 ml of methanol, 1.2 ml of water, and 15 ml of dimethyl sulfoxide at room temperature for 18 hours, the resulting reaction mixture did not give an nmr signal at -4.46 ppm, but it did give more intense absorptions in the olefinic region of the nmr spectrum. It

was concluded that the signals at -4.46 ppm and at -3.92 ppm were from the stereoisomers of 1-bromo-4-trichloromethyl-cis-decalin with axial and equatorial bromine, respectively.

b. In Methylene Chloride Solution

A methylene chloride solution (200 ml) of I (2.72 g, 0.02 mole) and bromotrichloromethane (3.96 g, 0.02 mole) under a nitrogen atmosphere was irradicated with 3500 Å light. The reaction was complete after 3.5 hours of irradiation. After the solvent had been removed on a rotary evaporator under reduced pressure, 6.6 g of crude products remained. The nmr spectrum of this reaction mixture was compared with the nmr spectrum obtained from the previous reaction mixture (excess bromotrichloromethane and without solvent). Both spectra exhibited similar features except for the relative areas of the signals due to the olefinic protons and these centered at -4.46 ppm and -3.92 ppm. There was more olefinic absorption in the spectrum of the excess bromotrichloromethane reaction mixture than in that of the one obtained in methylene chloride solution. When excess bromotrichloromethane was used, the ratio of the areas of the signals centered at -4.46 ppm and -3.92 ppm was 1 : 1.4, respectively, while the dilute methylene chloride solution led to a ratio of 1 : 4. The signal at -3.92 ppm had increased substantially in this latter spectrum. Attempts to determine the percentage of the components of the reaction products by gas chromatography was found to be unsatisfactory because of extensive decomposition. In summary, the major products from this reaction were 1-bromo-4-trichloromethyl-cis-decalins (XVI, and XVIII) with 4-trichloromethylbicyclo[4.4.0]dec-1-ene and 4-trichloromethylbicyclo[4.4.0]dec-2-ene present as minor products.

3. Radical Addition of Bromoform

A solution consisting of 5 g of I and 47 g of bromoform under nitrogen atmosphere was irradiated with 3500 Å light for 15 hours. The excess bromoform and unreacted starting material were then distilled off under vacuum, leaving 11.5 g of crude products. The nmr spectrum of this reaction mixture had signals in the olefinic region (-5 to -6 ppm), a doublet at -5.76 ppm (J = 4 Hz), a sextet centered at -3.95 ppm, and a complex multiplet between -1.0 and -3.00 ppm. The infrared spectrum of the mixture included absorption at about 14.2 μ, indicating the presence of the cis-alkene. Elution chromatography of 3 g of the mixture on 90 g of Florisil led to the isolation of one major product XXI, 1.7 g, from the middle collections. The infrared spectrum (Fig. 11) of XXI included absorptions at 14.49 and 14.93 μ, which can be attributed to the C-Br bond. The nmr spectrum (Fig. 12) of this adduct consisted of a doublet at -5.76 ppm (1H, J=4 Hz, -C<u>H</u>Br_2), a 6-line absorption at -3.95 ppm (1H, J=9.5, 2.5 Hz, C<u>H</u>Br), and a complex multiplet between -1.0 ppm and -3.00 ppm. The adduct was identified at 1-bromo-4-dibromomethyl-cis-decalin.

Anal. Calcd. for $C_{11}H_{17}Br_3$: C, 34.0; H, 4.4. Found: C, 34.3; H, 4.4.

The minor products were not isolated in pure state and were not studied in detail.

D. Ionic and Radical Additions of Reagents to cis,trans-1,5-Cyclodecadiene

1. Additions of Molecular Chlorine

a. In the Absence of Oxygen

To a three neck flask equipped with a condenser and drying tube was added 2.72 g (0.02 mole) of I and 100 ml of carbon tetrachloride. The reaction system was flushed with dry nitrogen gas. Chlorine (2.0 g) was condensed in a chilled finger condenser and was subsequently swept through a drying tube by a stream of dry nitrogen gas into the reaction flask. A 300 watt incandescent light bulb was used to initiate the reaction. The temperature of the reaction mixture was kept below 40°C by an ice-water bath. The reaction was complete within 10 minutes. The reaction mixture was washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent on a rotary evaporator at reduced pressure yielded 4.3 g of crude products. Gas chromatographic analysis of this residue with a Carbowax 20 M column (12' x 1/8", 140°) on a Beckman GC-5 instrument revealed that it was a mixture. About 80% of the total area of the reaction mixture chromatogram consisted of a peak with a shoulder of longer retention time. The nmr spectrum of this reaction mixture showed very little absorption due to olefinic protons. Distillation of the crude products at reduced pressure (0.2 mm Hg) gave 2.4 g in three distillate fractions [(1) 44-44.5°C, 0.7 g; (2) 70-74°C, 0.6 g; (3) 74-76°C, 1.1 g.] and 1.6 g of undistilled residue.

Fraction I of the above distillate contained one major component which was purified by preparative gas chromatography. The infrared spectrum (Fig. 13) is in the appendix section. The nmr spectrum (Fig. 14) of this compound includes a doublet at -5.52 ppm (1H, C=C<u>H</u>, J=1.5 Hz), a multiplet at -4.18 ppm (1H, -C<u>H</u>Cl), and multiplets between -1.30 and -2.80 ppm (13H, the rest of the protons). The structure of this

compound based on the spectral data is assigned as 5-chlorobicyclo-[4.4.0]dec-1-ene.

Fractions 2 and 3 were shown by temperature-programmed gas chromatography (90-160°, 5°/min) on a Carbowax 20 M column (12' x 1/8") to consist of two components in about equal amounts. No attempt was made to separate these two components. However, the infrared spectrum (Fig. 15) of these fractions show no absorptions due to olefinic double bond, and the ratio of the area of the downfield protons at -4.10 ppm (HCCl) and the upfield protons in the nmr spectrum (Fig. 16) is 1 : 7 or 2 : 14. These data suggest that the two compounds are isomeric 1,4-dichlorodecalins.

b. In the Presence of Oxygen

To a three neck flask equipped with a condenser and drying tube was added 2.72 g (0.02 mole) of I and 100 ml of carbon tetrachloride. Chlorine (2.0 g) was condensed in a chilled finger condenser and was subsequently swept through a drying tube by a stream of dry air into the reaction flask. The mixture was then allowed to stir at room temperature for two hours. The disappearance at this time of the yellowish color due to the chlorine was taken as evidence for the completion of the reaction. The reaction mixture was washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent on a rotary evaporator at reduced pressure yielded 4.4 g of crude products. Gas chromatographic analysis of the mixture showed one major peak with a shoulder of longer retention time. The area of this peak accounted for 80% of the total area of the reaction mixture chromatogram. The nmr spectrum of the reaction mixture showed very little absorption due to olefinic protons. No substantial difference was observed for this air sweep

and the nitrogen sweep reactions. The major products were also identified as 1,4-dichlorodecalins by comparing their retention times with the compounds obtained from (a).

2. Additions of Iodobenzene Dichloride

a. Iodobenzene Dichloride

Iodobenzene dichloride was prepared from iodobenzene and chlorine in chloroform solution as described by Lucas and Kennedy.[66] It was recrystallized from chloroform and air dried before use.

b. Addition of Iodobenzene Dichloride in the Presence of Oxygen

To a flask fitted with a magnetic stirrer and a condenser topped by a calcium chloride drying tube was added 1.36 g (0.01 mole) of I and 25 ml of carbon tetrachloride. Iodobenzene dichloride (2.75 g, 0.01 mole) was added to the solution in one portion. The mixture was then allowed to stir at room temperature for 4.5 hours. By that time, all of the crystalline iodobenzene dichloride had disappeared; that is, the solution had become homogeneous. The reaction mixture was washed with water and then dried over anhydrous magnesium sulfate. Gas chromatographic analysis of the reaction mixture with a Packard 700 instrument and a Ucon column (6' x 1/8", 160°) yielded the following data:

Retention time (min.)	12	12.8	14.0	30.2	32.4	34.4
Relative area (%)	23	13	13	19	27	5

The component with retention time of 12 minutes were identified as 5-chlorobicyclo[4.4.0]dec-1-ene by comparing its retention time with that of the compound obtained from the addition of molecular chlorine to I in the absence of oxygen (b.p. 44-44.5°, 0.2 mm). The components with retention times of 12.8 and 14.4 minutes were not studied in

detail. The components with retention times of 30.2 and 32.4 minutes were identified as 1,4-dichlorodecalins on the basic of gas chromatography.

c. Addition of Iodobenzene Dichloride in the Absence of Oxygen

A flask contained a mixture of I (1.36 g, 0.01 mole) and iodobenzene dichloride (2.75 g, 0.01 mole) in 25 ml of carbon tetrachloride was degassed by the freeze-thaw method and sealed. An exothermic reaction occured spontaneously when the reaction mixture warmed to room temperature (25°C). That the reaction was complete in a few seconds was evident by the disappearance of the crystalline iosobenzene dichloride to give a homogeneous solution. After cooling to room temperature, the reaction flask was opened. The reaction mixture was washed with water and then dried over anhydrous magnesium sulfate. Gas chromatographic analysis of the reaction mixture under the same conditions as in (b) gave the following data:

Retention time (min.)	12	12.8	14.0	30.2	32.4	34.4
Relative area (%)	17	18	17	15	29	4

The identifications of the first, fourth, and fifth components as 5-chlorobicyclo[4.4.0]dec-1-ene and 1,4-dichlorodecalins were based on retention times of these components as in the previous case.

3. Additions of Bromine Azide

a. Preparation of Bromine Azide

Bromine azide was prepared immediately before use by the method of Hassner and Boerwinkle.[23] For ionic addition, 8.0 g of bromine was added to an ice-cooled, stirred mixture of 32.5 g of sodium azide,

100 ml of methylene chloride, and 25 ml of 30% hydrochloric acid. The heterogenous mixture was stirred for 30 minutes, after which time the solution lightened considerably in color. The methylene chloride solution was separated from the water phase and used in the addition. For radical addition, the same procedure was used except that pentane (400 ml) was used instead of methylene chloride, and the pentane solution of bromine azide was purged with nitrogen.

b. Ionic Addition of Bromine Azide

A solution of bromine azide (25 mmoles) in methylene chloride (100 ml) was added to a solution of 3.2 g (23.2 mmoles) of I in 200 ml of nitromethane at 0°C. The solution was stirred for one hour. The solvent was removed under reduced pressure to leave 6 g of yellow oil. The infrared spectrum of the oil showed strong absorption at 4.75 μ, indicative of an azido functional group, but no absorptions attributable to the carbon-carbon double bond stretching. The nmr spectrum of the oil was devoid of olefinic proton absorptions, but it did include a complex multiplet between -3.25 and -4.65 ppm, which is in the range of protons geminal to a bromo or an azido substituent in the cyclohexane ring system. The product is identified as 1-bromo-4-azidodecalin.

c. Radical Addition of Bromine Azide

A pentane solution (400 ml) of bromine azide (25 mmoles) was added to a solution of 3.2 g (23.2 mmoles) of I in 100 ml of pentane at 0°C. After one hour stirring, the solvent was removed to give 6 g of yellow oil. The infrared spectrum of the oil again had atrong absorption at 4.75 μ, due to the azido group. The nmr spectrum of the oil included some olefinic proton absorptions (5-6 ppm), and, like the spectrum of

the ionic reaction product, it had complex overlapping signals between -3.25 and -4.65 ppm. The complicated signals, however, do not allow one to compare in detail the ionic and radical processes at the moment.

E. Additions of Carbenes to cis,trans-1,5-Cyclodecadiene

1. Methyleneation by Simmons-Smith Reaction[47]

To a flask, equipped with a magnetic stirrer and a condenser with a drying tube, was added 8.6 g (0.132 g. at.) of zinc-copper couple and 40 ml of anhydrous ethyl ether. A small crystal of iodine was added, and the mixture was stirred for 15 minutes. The reddish color due to iodine disappeared. To the stirring mixture was added 18 g. (0.132 mole) of I and 35 g. of methylene iodide. The reaction mixture was then stirred at reflux temperature for 24 hours. The zinc iodide crystals and copper metal formed in the reaction were separated by filtration. The filtrate was hydrolyzed with 1 M hydrochloric acid and diluted with 100 ml of water. The solution was extracted 3 times with pentane. The pentane solution was washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent yielded 19.5 g of a slightly yellow liquid. Analysis of the crude product by gas chromatography indicated that there were two major products (60%) in the mixture in addition to the unreacted diene I, its thermal isomerization product, cis-1,2-divinylcyclohexane, and methyl iodide. The gas chromatography area ratio of the two products was 89 : 11. The major component was isolated by preparative gas chromatography and was identified on the basis of spectroscopic data as trans-bicyclo[8.1.0]cis-undec-5-ene. Its nmr spectrum consists of multiplets

at -5.40 ppm (2H, C<u>H</u>=C<u>H</u>), at -1.30 to -2.5 ppm (12H), at -0.48 ppm (2H, bridgehead protons, and at -0.10 ppm (2H, CH_2 of the cyclopropane ring). The infrared spectrum of the adduct has strong absorption at 14.2 μ (<u>cis</u> C=C) but only minimal absorption at 10.4 μ (<u>trans</u> C=C).

2. <u>Methyleneation by Diazomethane</u>

A flask containing 7 ml of 50% aqueous potassium hydroxide solution and 50 ml of ethyl ether was cooled in an ice-salt bath, and 3.5 g of <u>N</u>-methyl-<u>N</u>-nitrosourea[67] was added in small portions while the temperature of the reaction system was kept below 0°C. Each successive addition was delayed until the added solid materials had disappeared completely. A yellow ether solution was obtained when all the <u>N</u>-methyl-<u>N</u>-nitrosourea had been added to the basic solution. The diazomethane content in the ether solution was not assayed, but the literature reports that the yield should amount to about 1.0 to 1.1 g.[48] The ether layer was separated from the aqueous solution and was used for the following addition reaction without further purification.

To a round bottom flask fitted with a condenser and a drying tube was added 3.5 g of I. The diazomethane-ether solution prepared above was added with stirring in one portion, and 0.5 g of copper powder was added. The stirred reaction mixture was maintained at 0.5°C by cooling in an ice-salt bath. After 3 hours, the cooling bath was removed and the reaction mixture was stirred overnight. At the end of that time, a few drops of acetic acid were added

to the reaction mixture; no nitrogen gas evolution could be observed. The copper was separated by filtration, and the reaction mixture was washed first with sodium bicarbonate solution and then with water. After the ether solution had been dried with anhydrous magnesium sulfate, the solvent was removed on a rotary evaporator, yielding 3.6 g of product mixture. Gas chromatographic analysis of the mixture revealed that a small amount of bicyclo[8.1.0]undecenes had formed. These alkenes were identified by gas chromatographic comparison with the methyleneation products from the Simmons-Smith reaction as trans-bicyclo[8.1.0]-cis-undec-5-ene and cis-bicyclo[8.1.0]-trans-undec-5-ene. The area ratio of these two components was 73 : 27.

3. Addition of Dibromomethylene.[49]

A flask fitted with a stirrer and a condenser was flushed with nitrogen and charged with 4.2 g of potassium t-butoxide and 4.4 g of I in 50 ml of pentane. A dropping funnel was charged with 8.5 g of bromoform, and the flask was cooled in an ice-salt bath. The bromoform was added dropwise to the stirred slurry. The color of the reaction mixture changed gradually from light yellow to tan. The mixture was then allowed to come to room temperature and was stirred overnight. The mixture was poured into ice-water and extracted several times with pentane. After the combined pentane extract had been washed with water, it was dried over anhydrous magnesium sulfate. Removal of the solvent on a rotary evaporator yielded 6.6 g of crude product. Distillation of the product mixture under vacuum (0.6 mm) gave 5.3 g in

four distillate fractions [1) 25-32°C, 2.7 g; 2) 32-104°C, 0.1 g; 3) 104-114°C, 2.1 g; 4) 114-117°C, 0.4 g] and 1.3 g of undistilled residue. Fraction 1 contained the unreacted diene I and bromoform. Fractions 2 through 4 contained two other major components. The undistilled residue contained the same products obtained in fraction 4. The total yield of the addition products in all fractions was about 70-75%. The ratio of the major and the minor products was about 75 : 25. The major component of the reaction products was isolated by preparative gas chromatography. The infrared spectrum (Fig. 17) of the adduct includes absorptions at 3.28 (m), and 14.25 (S) μ, indicative of the presence of a cis double bond. The nmr spectrum (Fig. 18) consists of multiplets at -5.40, -2.25, -1.65 and -1.15 ppm, and the ratios of the intensities of these signals are 2 : 8 : 4 : 2, respectively. The structure of the compound assigned on the basis of these data is trans-11,11-dibromobicyclo[8.1.0]-cis-undec-5-ene.

4. Addition of Isopropylidenemethylene

The precursor of isopropylidenemethylene, 5,5-dimethyl-N-nitrosooxazolidone, and the base lithium 2-ethoxyethoxide were prepared according to the detailed procedures supplied by Professor M. S. Newman. [68]

A stirred mixture of 5.0g (0.035 mole) of 5,5-dimethyl-N-nitrosooxazolidone in 20 ml of dry I at 45-50°C was treated in three equal portions with 5.0 g (0.051 mole) of lithium 2-ethoxyethoxide. Each addition caused vigorous nitrogen evolution. After stirring at room temperature for 30 minutes, the reaction mixture was poured into ice-water. The products were extracted into ethyl ether. The combined ether solution was washed with saturated salt solution and was dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator, and the unreacted diene I was distilled at 51-53°C (5 mm) to leave 5.6 g of yellow oil. This mixture was shown by gas chromatography to include two major components (90 area %) in the area ratio of 70 : 30, with the shorter retention time component being the predominant one. The yield of these two compounds extimated from the area of the gas chromatogram was about 75%. Distillation of the oily material at 71-73°C (0.7 mm) yielded 2.0 g of a slightly yellow liquid, which was shown by gas chromatography to consist of two components in the area ratio of 84 : 16. The undistilled residue also contained mainly the same components in the area ratio of 60:40.

The major product of the reaction was obtained by preparative gas chromatography of the distilled fraction (6' x 1/4" column, 30% SE-30 silicone on chromosorb P, 140°C). The infrared spectrum (Fig. 19) of XXV_c includes absorptions at 5.61 μ (C=C), and 14.20 μ (cis C=C); the nmr spectrum of XXV_c (Fig. 20) consists of a multiplet at -5.40 ppm

(2H, CH=CH, a sharp singlet at -1.70 ppm (6H, -CH_3), a broad signal at -0.95 ppm (2H, cyclopropane ring protons), and a complex multiplet between -1.4 and -2.5 ppm (12H, the rest of the protons). Another component present in the reaction mixture was also isolated by preparative gas chromatography. The infrared spectrum (Fig. 21) of the minor product is also different from that of the major product in that is has absorption at 10.4 μ, which is due to the trans-alkene. The nmr spectrum (Fig. 22) of this component differs from that of the major product in that the downfield signal due to olefinic protons is a -5.55 ppm, the signal at -1.70 ppm is a two line pattern here rather than a singlet, and the upfield signal appears at -1.25 ppm rather than at -0.95 ppm. These two products were identified as 11-isopropylidenebicyclo[8.1.0]-cis-undec-5-ene (XXV_c) and 11-isopropylidenebicyclo[8.1.0]-trans-undec-5-ene ($XXVI_c$).

F. Photoisomerization of 1,5-Cyclodecadienes

1. General Procedure

A solution of cis,trans-1,5-cyclodecadiene (I) or cis,cis 1,5-cyclodecadiene (XLIII) with appropriate catalyst or sensitizer in ethyl ether solution was irradiated inside a Rayonet Photochemical Reactor. The quartz reaction flask (equipped with a condenser and a drying tube) was surrounded by 16 R.P.R. 2537 Å lamps. All photochemical reactions were carried out under a nitrogen atmosphere. The progress of the isomerization of I to XLIII or XLIII to I was followed by gas chromatography; on a Carbowax 20 M column, I has a shorter retention time than XLIII. The reaction was stopped when the ratio of the isomeric dienes I and XLIII did not change further (photostationary state).

2. Copper(I) Chloride Catalyzed Photoisomerization of cis,trans-1,5-Cyclodecadiene.

When copper(I) chloride[69] (0.1 g) was added to a solution of 5 g of I in 250 ml of ethyl ether, the resulting mixture became cloudy. The mixture was subjected to ultraviolet light. After 22.5 hours, some new product was detected by gas chromatographic and nmr analysis. Since some green precipitate had formed, the reaction mixture was filtered, and the flask was cleaned with nitric acid. The ether solution filtrate was returned to the flask and was irradiated for an additional 42.2 hours. A check by gas chromatography revealed that about 1/3 of I had been converted to XLIII. The reaction mixture was again filtered and returned to the cleaned flask. The procedure was repeated again after a total reaction time of 95 hours, and 50 mg of fresh copper(I) chloride was added. After 120 hours total irradiation time, the ratio of I and XLIII was estimated to be 1 : 4 by gas chromatography (relative area). Further irradiation did not change the ratio of I and XLIII in the reaction mixture, and the reaction was stopped.

The solvent was removed, and the concentrated reaction mixture was distilled through a 10 cm column at reduced pressure (4.8 mm Hg). Five fractions were collected: (I) 0.2 g, b.p. 25-30°; (2) 0.2g, 48-51°; (3) 0.4g, 51-53°; (4) 0.5g, 53-54°; (5) 3.2g, 54-56°. The undistilled material (0.3g) was discarded. Fraction 1 contained mainly cis-1,2-divinylcyclohexane and ether. The identity of cis-1,2-divinylcyclohexane was determined by comparing its infrared and nmr spectra and gas chromatography data with those of an authenic sample obtained from the Cope rearrangement of I. Fraction 3 contained mainly I. Fraction 5 was estimated by gas chromatography to be about 95% XLIII. Separation of I and XLIII

by preparative gas chromatography (12 ft. Carbowax 20 M column, column temperature 80°, inlet temperature 140°) appeared to be the most convenient method. The diene XLIII had a retention time 4 minutes longer than diene I (retention time 16 min.) under these conditions. The infrared spectrum (Fig. 23) of the diene XLIII included absorptions at 14.0 and 13.52 μ, characteristic of cis-alkene and was devoid of trans-alkene absorptions at 10.43 and 10.02 μ, which are present in the spectrum of the diene I. The nmr spectrum (Fig. 24) of the diene XLIII consisted of four distinct absorption areas: a complex multiplet centered at -5.38 ppm (C=CH, 4H), a multiplet centered at -2.34 ppm ($C=CCH_2$ $-CH_2$ -C=C, 4H), a multiplet centered at -2.16 ppm (other CH_2 -C=C, 4H), and a multiplet centered at -1.50 ppm (C-8 and C-9 protons, 4H). That these absorptions correspond to the signal of the protons as indicated was confirmed by spin decoupling experiments (Fig. 25). The mass spectrum of XLIII was very similar to that of I. It was characterized by the presence of m/e of 136, as expected for the parent ion of XLIII, and intense peaks of m/e = 27, 28, 29, 41, 53, 54, 67, and 79. These spectral data identify XLIII as cis,cis-1,5-cyclodecadiene.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.2; H, 11.8. Found: C, 87.9; H, 11.6.

3. Photoisomerization of cis,trans-1,5-Cyclodecadiene with Xylene Sensitizer.

A solution containing 2 ml of the diene I (98% pure) and 3 ml of xylene in 200 ml of ethyl ether was irradiated under a nitrogen atmosphere as described above. The progress of the reaction was followed by periodic sampling and gas chromatographic analysis. The ratio of I and XLIII in the reaction mixture as a function of time is tabulated in Table V (p. 47). Like the CuCl catalyzed reaction, two high boiling

materials were also formed in small amount but were not identified.

4. Photoisomerization of cis,cis-1,5-Cyclodecadiene with Xylene Sensitizer.

A solution composed of 2 ml XLIII (98% purity) and 3 ml of xylene in 200 ml of ethyl ether was irradiated as before. The major components of the mixture were I and XLIII after 28.6 hours of irradiation. The ratio of I and XLIII in the reaction mixture was about 1 to 4. An additional 19 hours of irradiation did not change the ratio of I and XLIII. However, the longer irradiation increased the proportion of high boiling products. Establishment of the photostationary state between I and XLIII was presumed, and the reaction was stopped.

G. Thermal Rearrangement of cis,trans- and cis,cis-1,5-Cyclodecadienes

When 1 g samples of I and XLIII in separate tubes were heated in an oil bath at 125±2°C, the thermal rearrangement of I and XLIII to cis-1,2-divinylcyclohexane (XLIV) occurred. Samples were taken from the reaction mixtures periodically and analyzed by gas chromatography. The extents of rearrangement of I and XLIII to XLIV as a function of time are tabulated in Table VI (p. 50).

The structure of the thermal rearrangement product of I and XLIII was identified as XLIV by comparison of its nmr spectrum and gas chromatogram with those of an authentic sample obtained from the thermal rearrangement of I.

H. Addition of Trifluoroacetic Acid to cis,cis-1,5-Cyclodecadiene

When 1 g of cis,cis-1,5-cyclodecadiene (XLIII) was added to 5 ml of trifluoroacetic acid, the temperature of the mixture rose to 48°C in one minute and began to drop a few minutes later. After work up,

the yield of cis-1-trifluoroacetoxy-cis-decalin (II) was estimated by gas chromatography to be 80% based on the amount of XLIII used. Some starting diene remained unreacted. The identification of the addition product as II was based on the gas chromatographic, infrared, and nmr data. Further verification was accomplished by hydrolyzing the addition product to the known cis,cis-1-decalol.[27,28]

I. Relative Rates of Additions of Trifluoroacetic Acid to cis,trans- and cis,cis-1,5-Cyclodecadiene.

To separate nmr tubes, each containing 0.2 ml of trifluoroacetic acid, was added 0.1 ml of I or 0.1 ml of XLIII. The progress of each reaction was followed by integrating the nmr signal in the olefinic region after 6 minutes of reaction time. With I, it appeared that the reaction was about 90% complete, but with XLIII, the reaction appeared to be only about 50% complete.

CHAPTER V

CONCLUSIONS

The additions of ionic reagents with cis,trans-1,5-cyclodecadiene (I) to give the transannular addition products, monosubstituted or disubstituted cis-decalins, are best explained by a concerted or stepwise mechanism such as the one proposed in scheme 1 (p. 12). These reactions provide useful synthetic means to convert the readily accessable cis, trans-1,5-cyclodecadiene into substituted cis-decalins with known stereochemistry.

The radical additions of reagents to cis,trans-1,5-cyclodecadiene to give the substituted decalins as products provide the first example of transannular radical cycloadditions in the cyclodecadiene systems. A step-wise mechanism such as the one proposed in scheme 5 (p. 28) is proposed for these reactions. The similarity of the results obtained from the ionic and radical additions of molecular chlorine or iodobenzene dichloride suggests that the factor which controls the product formation after the ring closure step is the same in both cases. From the study of models, the steric factor is probably the most important one in the conversion of substituted decalyl radicals such as XX to products.

The high selectivity of the cis-addition reagents for the trans carbon-carbon double bond to give 1,2-addition products is best explained by consideration of the eclipsing strain in the transition state. Models suggest that there is more eclipsing strain in the transition state when the cis-alkene is attacked than when the trans-alkene is attacked.

The diene I appears to be a useful probe of olefin addition mechanisms: reagents which add to both carbons in the alkene linkage at the same time

give substituted cyclodecenes as products, while reagents which add to the alkene carbons in steps produce substituted cis-decalins as products.

Photoisomerizations of cis,trans- and cis,cis-1,5-cyclodecadienes appear to be limited to the commonly observed cis,trans-isomerization processes without C=C migration or intramolecular cyclization. Nevertheless, the reaction with I provides an easy way of obtaining the cis,cis-isomer, which was previously unreported and would be hard to synthesize by any other means. The relative thermal stabilities of these two isomers in the Cope rearrangements and their relative rates of addition of trifluoroacetic acid result from conformational control of the transition states leading to the products.

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4. L.J. Bellamy, "The Infra-red Spectra of Complex Molecules", 2nd ed., John Wiley and Sons, Inc., New York, N.Y. 1958.

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APPENDIX

In this section, the infrared and nmr spectra (Figure 1-25) of some new compounds are accumulated in the order of citation in the body of this dissertation. Infrared spectra were recorded on Beckman IR-10 spectrometer: the spectrum of a liquid sample was taken on pure liquid between sodium chloride plates, and the spectrum of a solid sample was taken with a potassium bromide pellet. Nmr spectra of $CDCl_3$ or CCl_4 solutions were recorded on Varian Associates HA-60 or HA-100 instrument with tetramethylsilane (TMS) as internal reference.

The meanings of the labels in Figure 25, the decouple nmr spectra of cis,cis-1,5-cyclodecadiene, are as follow: Peak identities are indicated by Roman numerals (I-IV), and decouple scans at different irradiating frequencies are indicated by subscripts (A-D). Apparent chemical shifts (downfield from TMS, in Hz) are shown by arabic numerals without beat patterns, and the irradiating frequencies by arabic numerals preceded by beat patterns.

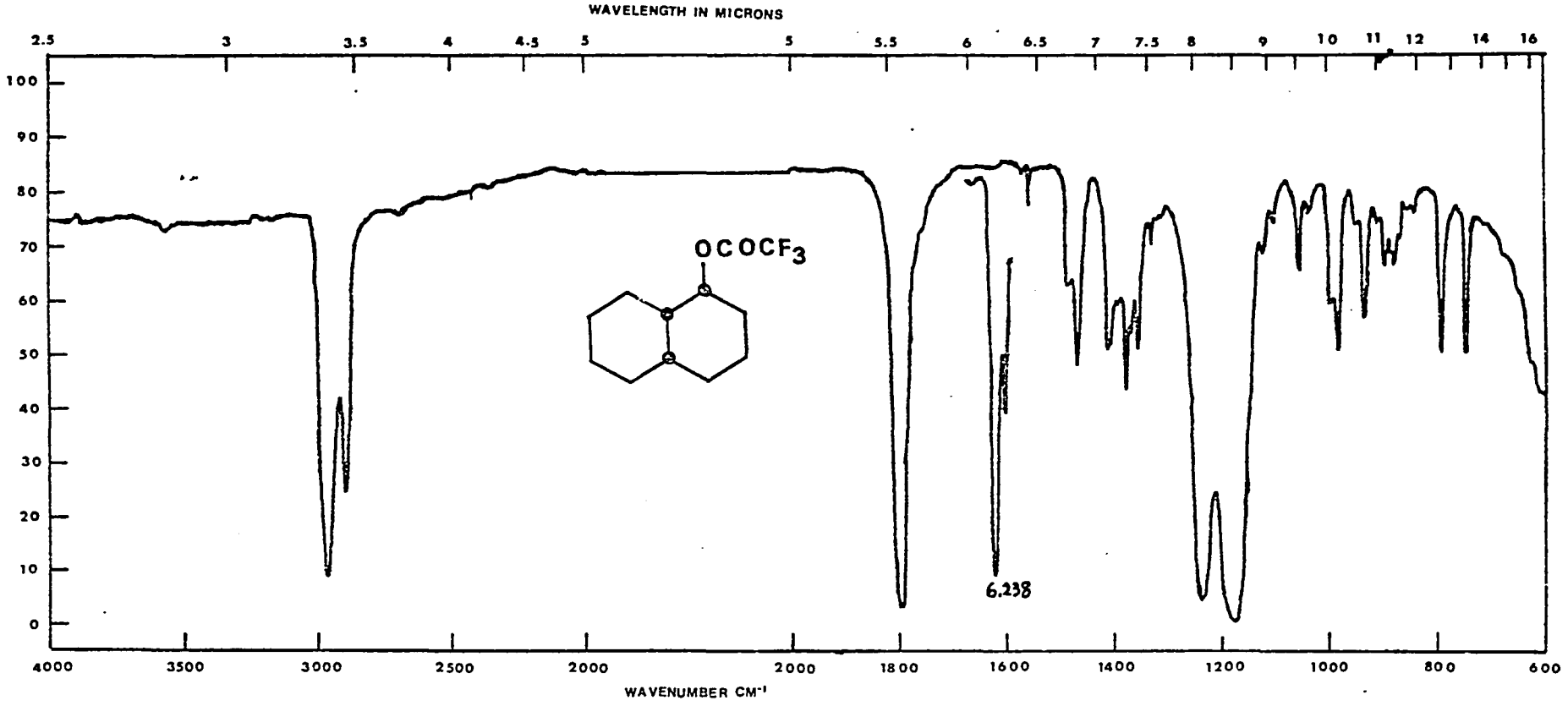

Figure 1. Infrared spectrum of cis-1-trifluoroacetoxy-cis-decalin(II) (neat, sodium chloride plates).

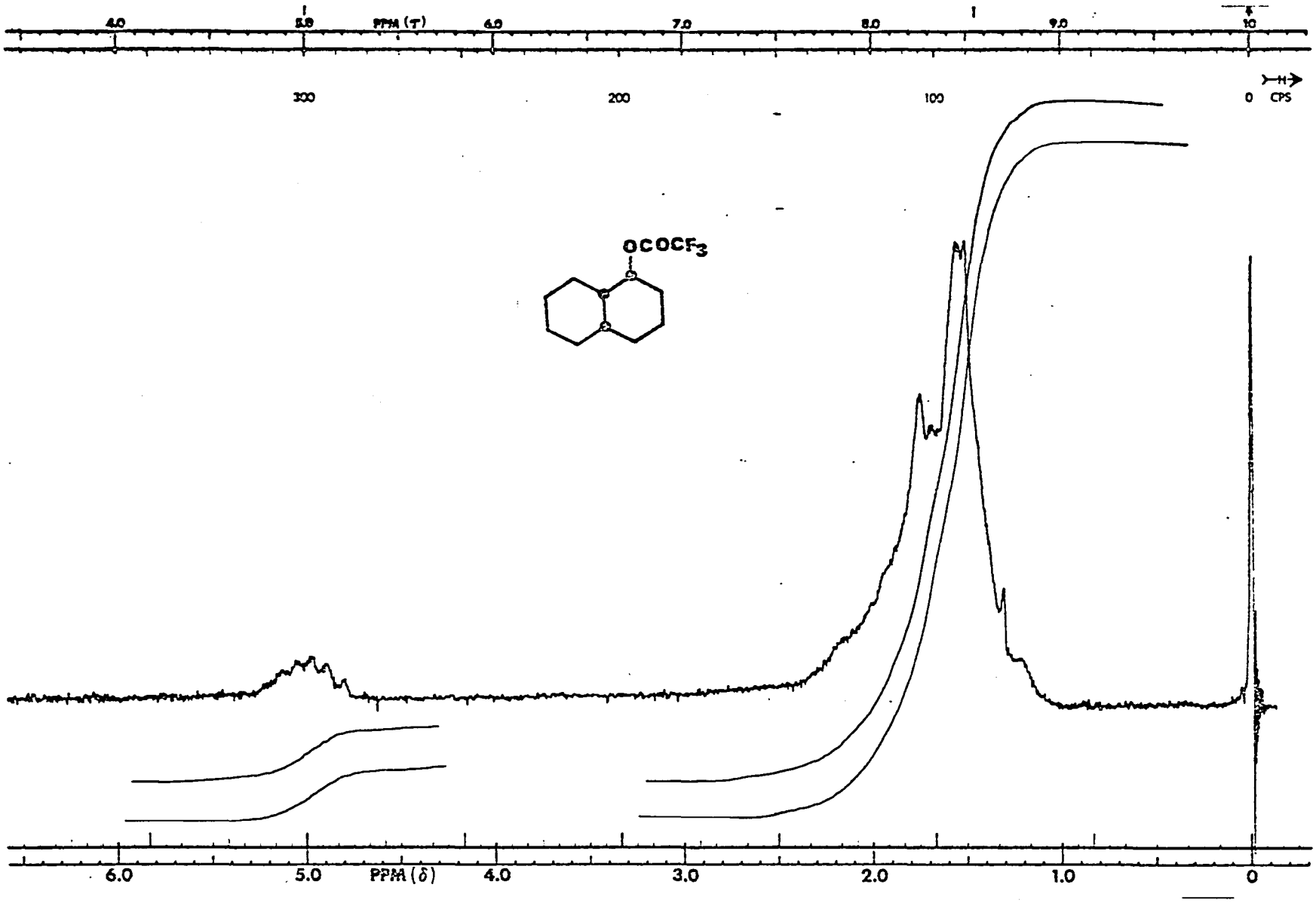

Figure 2. Nmr spectrum of cis-1-trifluoroacetoxy-cis-decalin (II) in CCl_4 at 60 MHz.

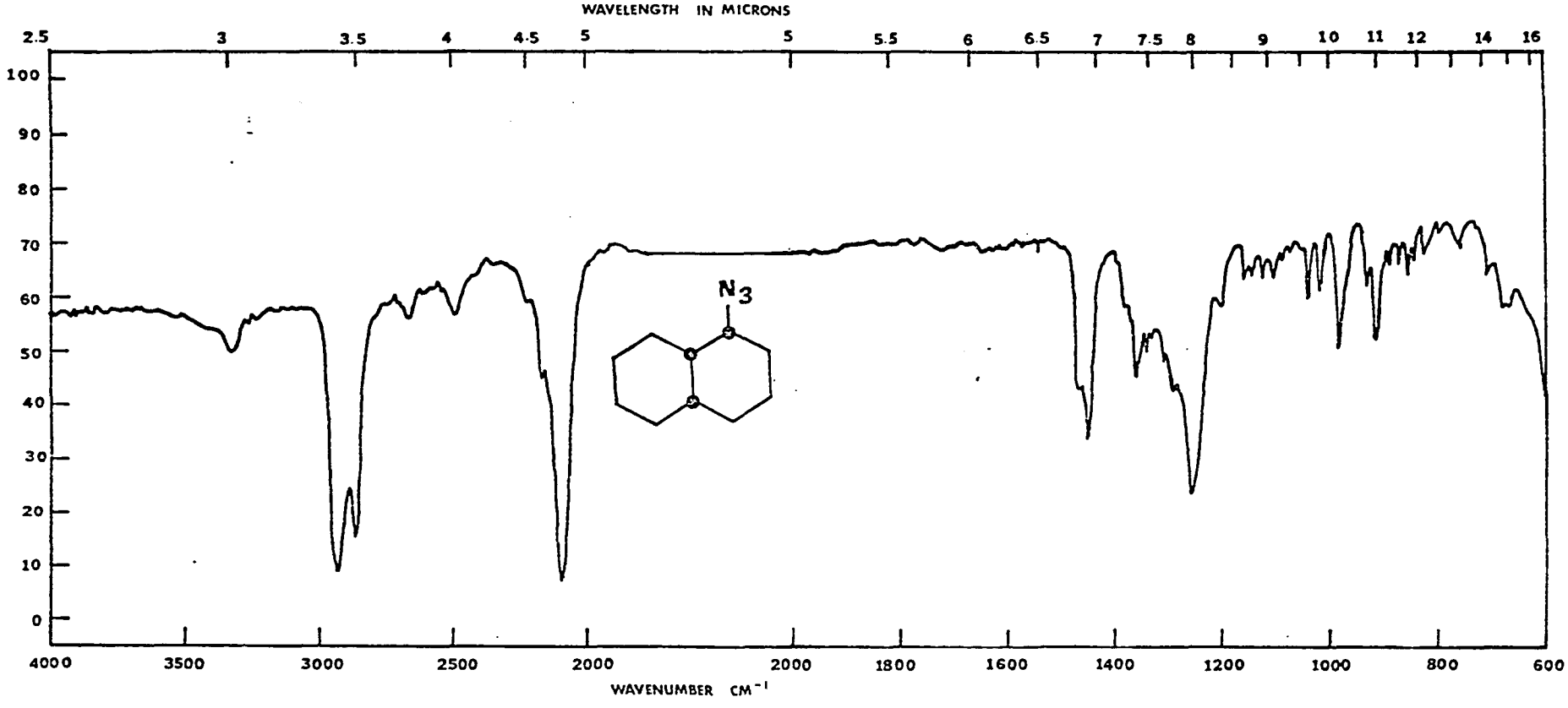

Figure 3. Infrared spectrum of cis-1-azido-cis-decalin (V). (Neat, sodium chloride plates.)

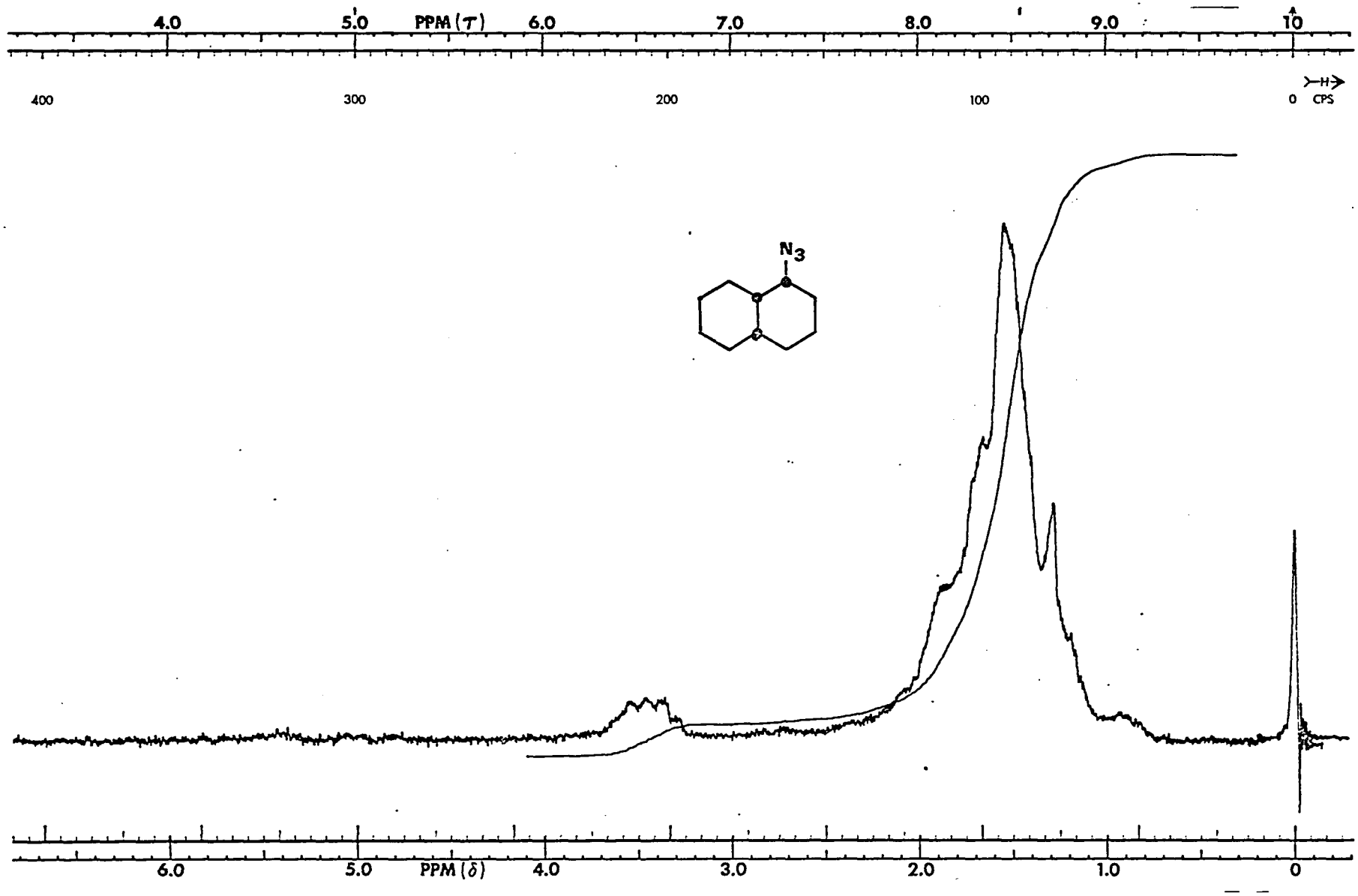

Figure 4. Nmr spectrum of cis-1-azido-cis-decalin (V) in CCl_4 at 60 MHz.

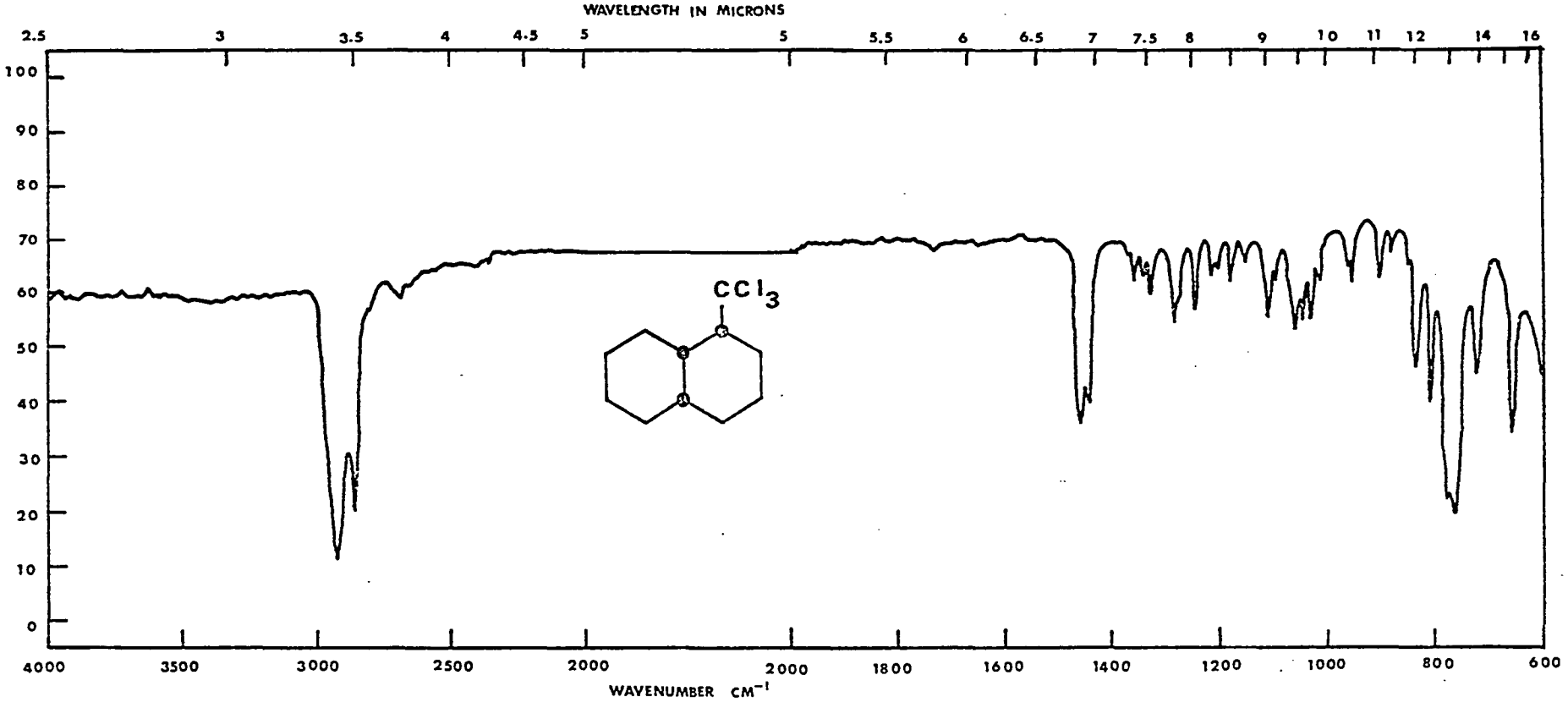

Figure 5. Infrared spectrum of 1-trichloromethyl-cis-decalin (XI) (neat, sodium chloride plates).

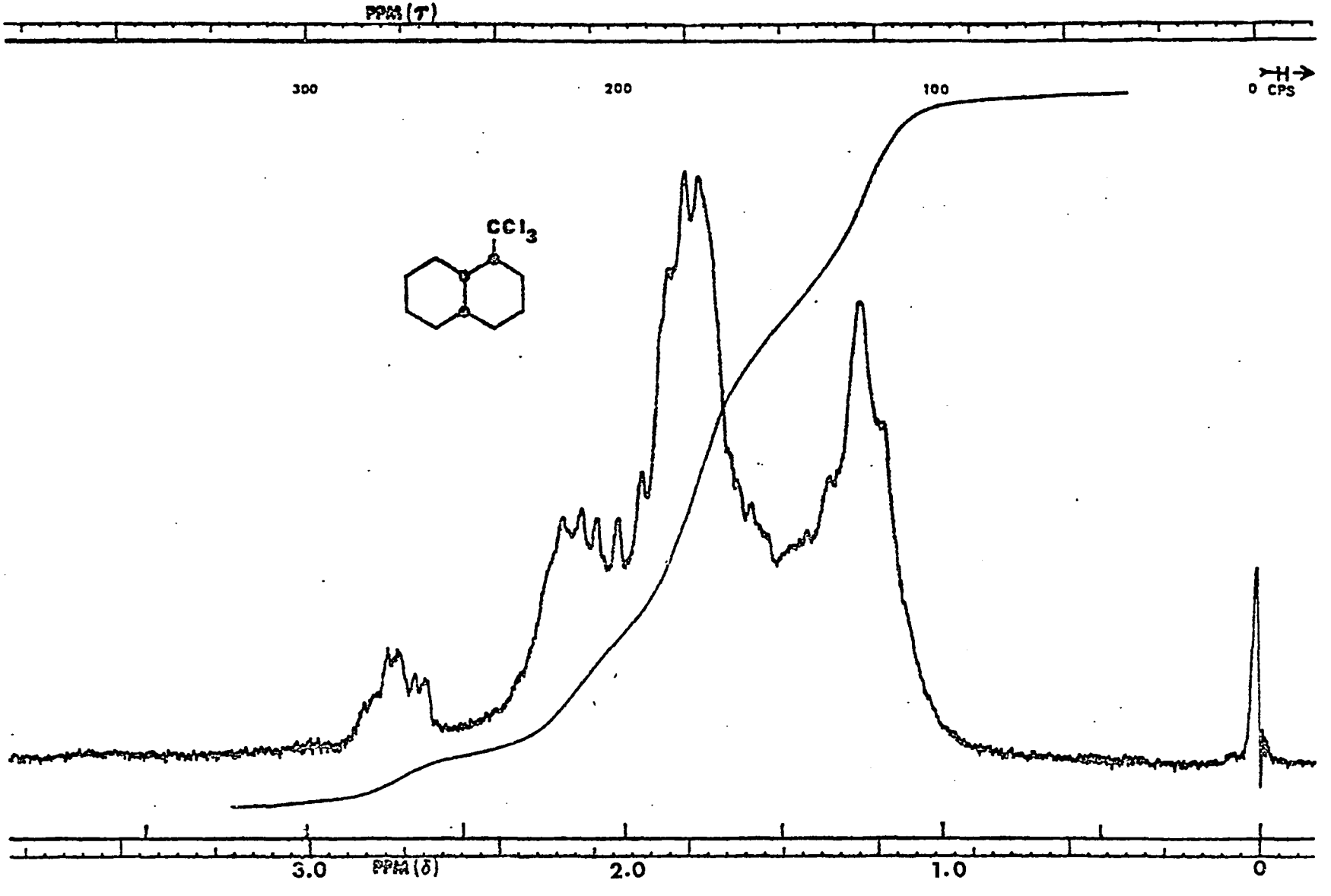

Figure 6. Nmr spectrum of 1-trichloromethyl-cis-decalin (XI) in CCl_4 at 100 MHz.

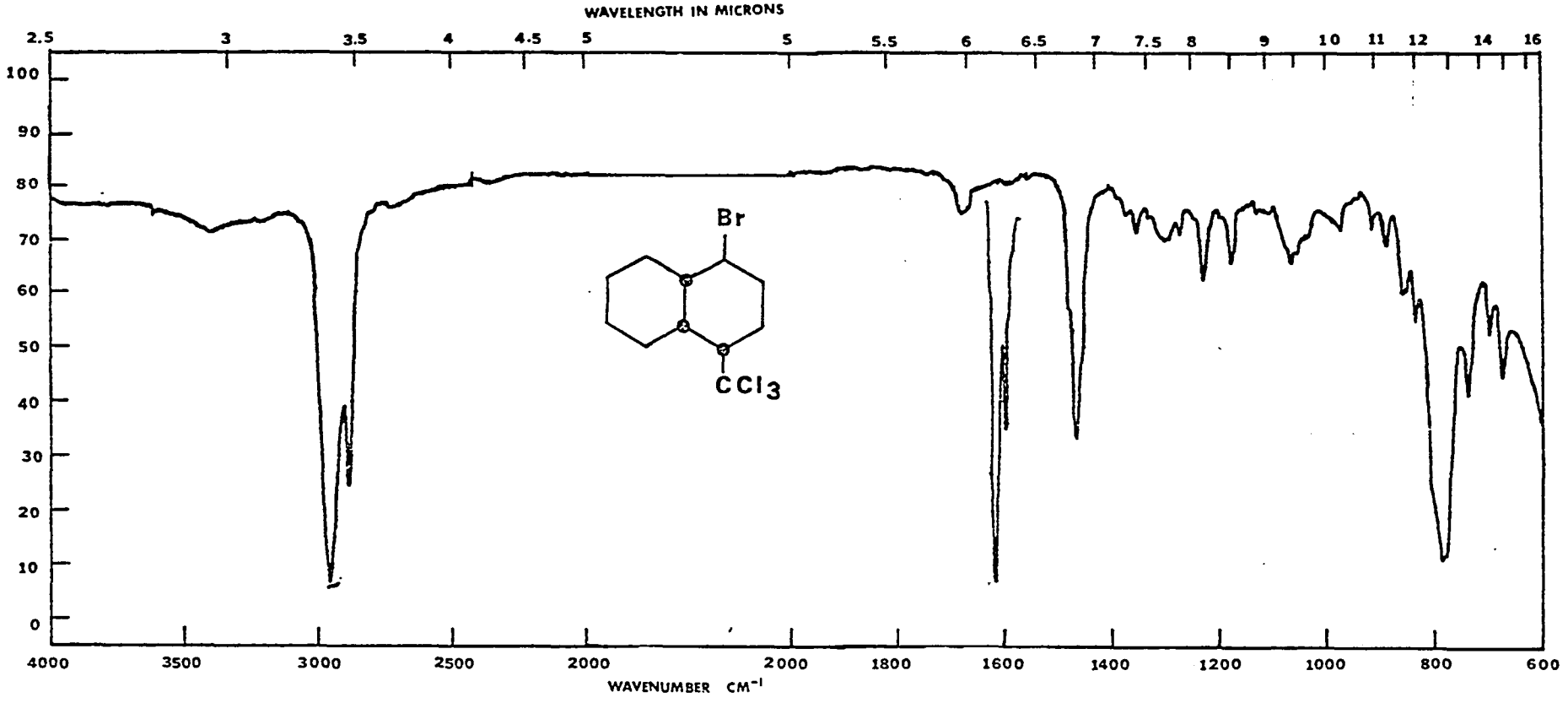

Figure 7. Infrared spectrum of 1-bromo-4-trichloromethyl-cis-decalin (XVI) (KBr).

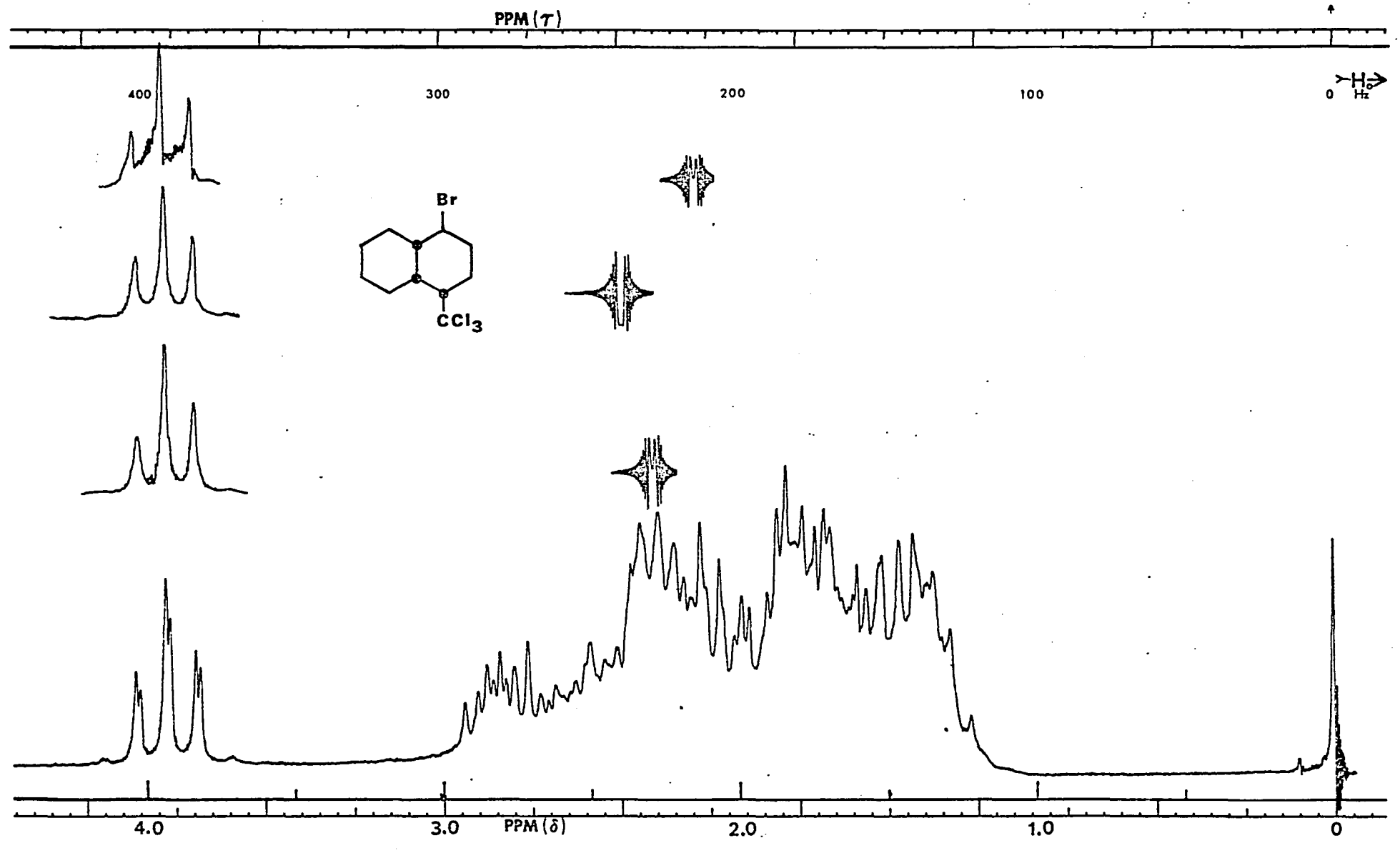

Figure 8. Nmr spectrum of 1-bromo-4-trichloromethyl-cis-decalin (XVI) in $CDCl_3$ at 100 MHz.

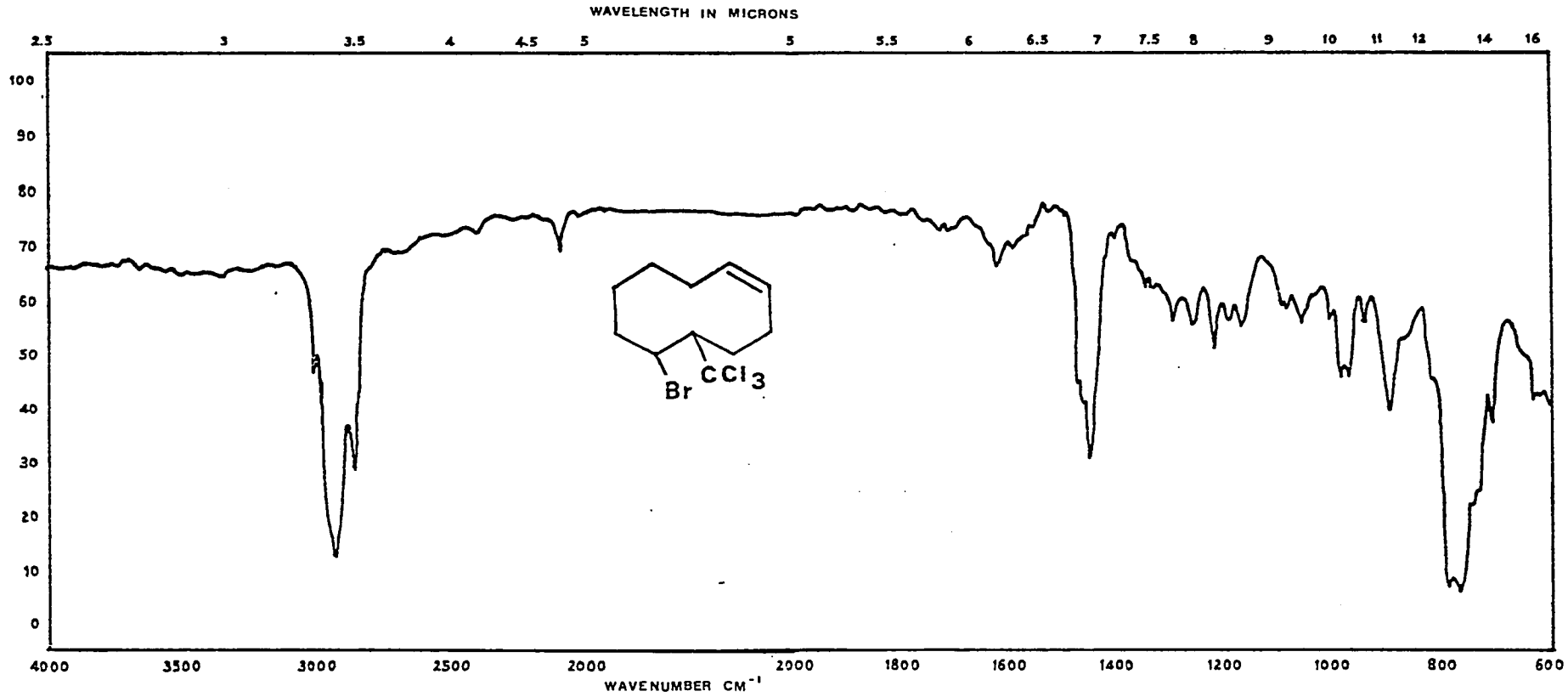

Figure 9. Infrared spectrum of 5-trichloromethyl-6-bromo-cis-1-cyclodecene (XVII). (Neat, sodium chloride plates.)

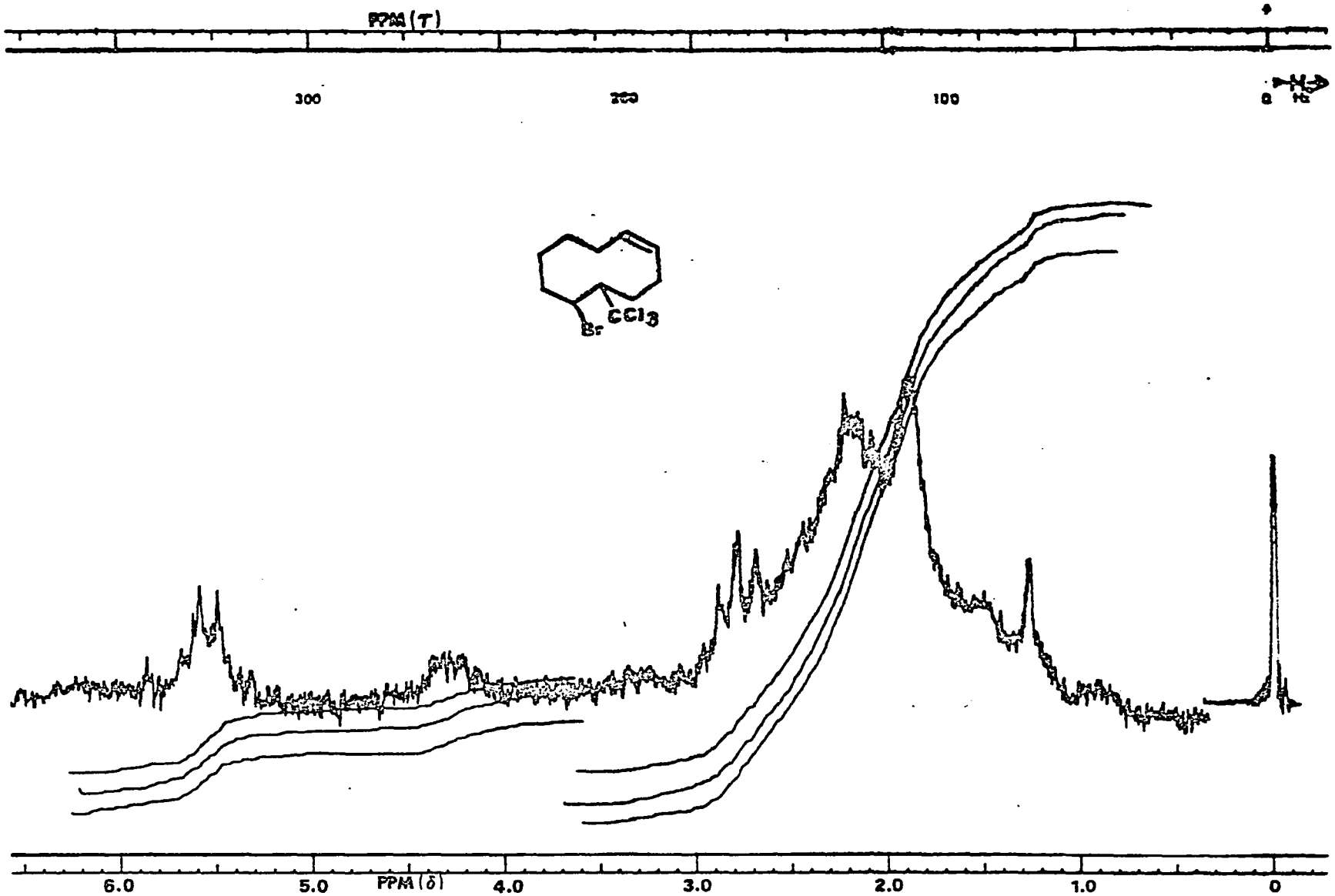

Figure 10. Nmr spectrum of 5-trichloromethyl-6-bromo-cis-1-cyclodecene (XVII) in CCl_4 at 60 MHz.

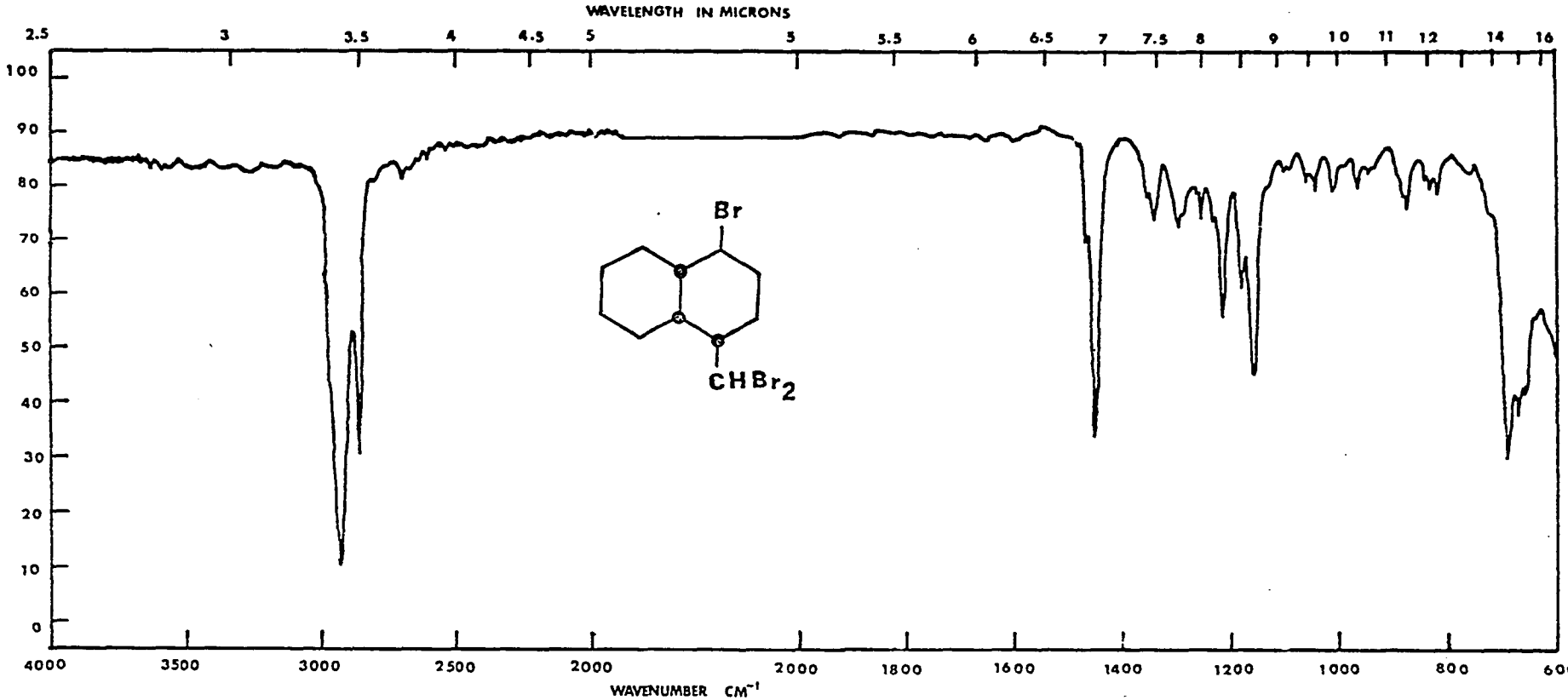

Figure 11. Infrared spectrum of 1-bromo-4-dibromomethyl-cis-decalin (XXI) (neat, sodium chloride plates).

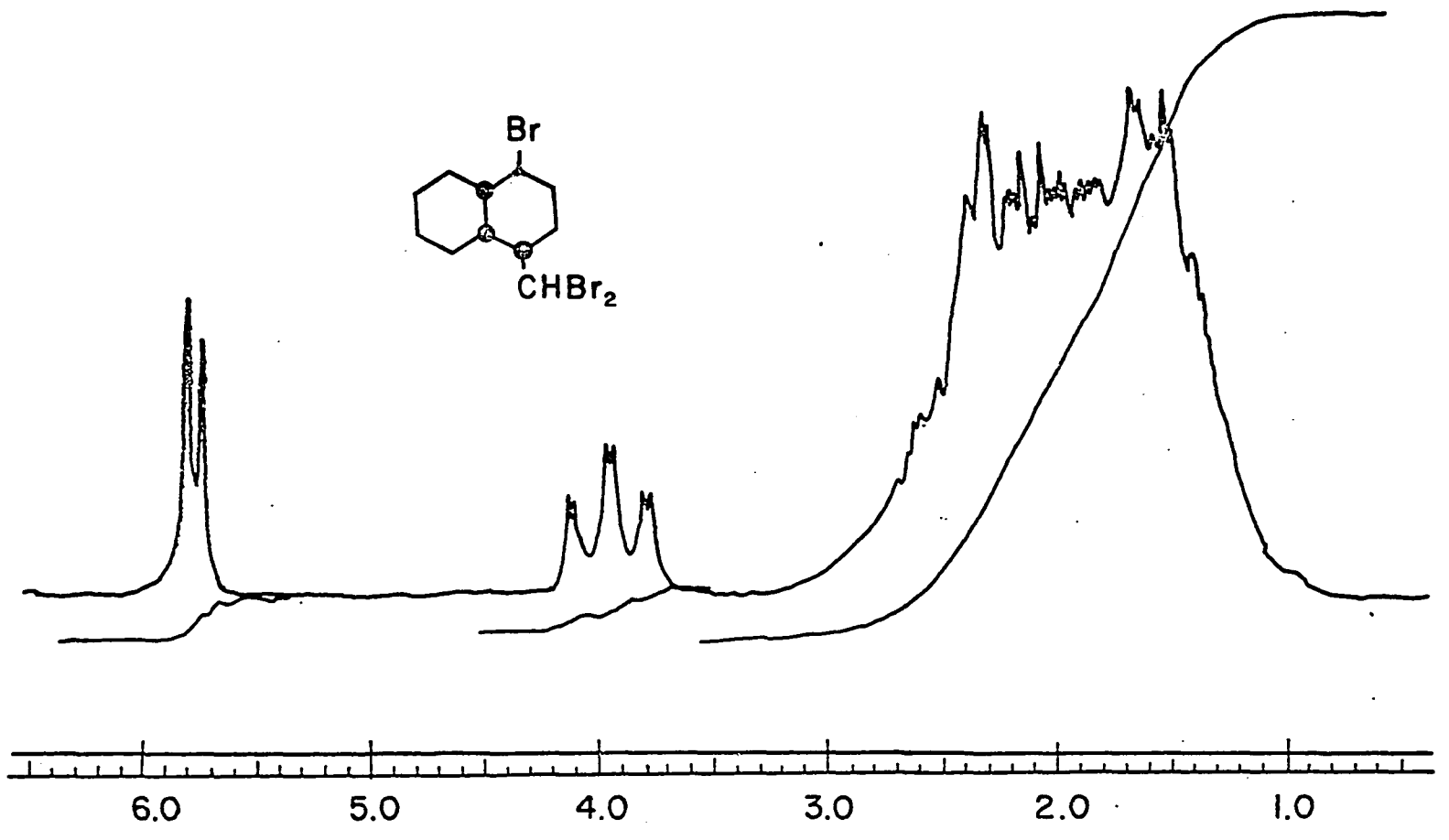

Figure 12. Nmr spectrum of 1-bromo-4-dibromomethyl-cis-decalin (XXI) in CCl_4 at 60 MHz.

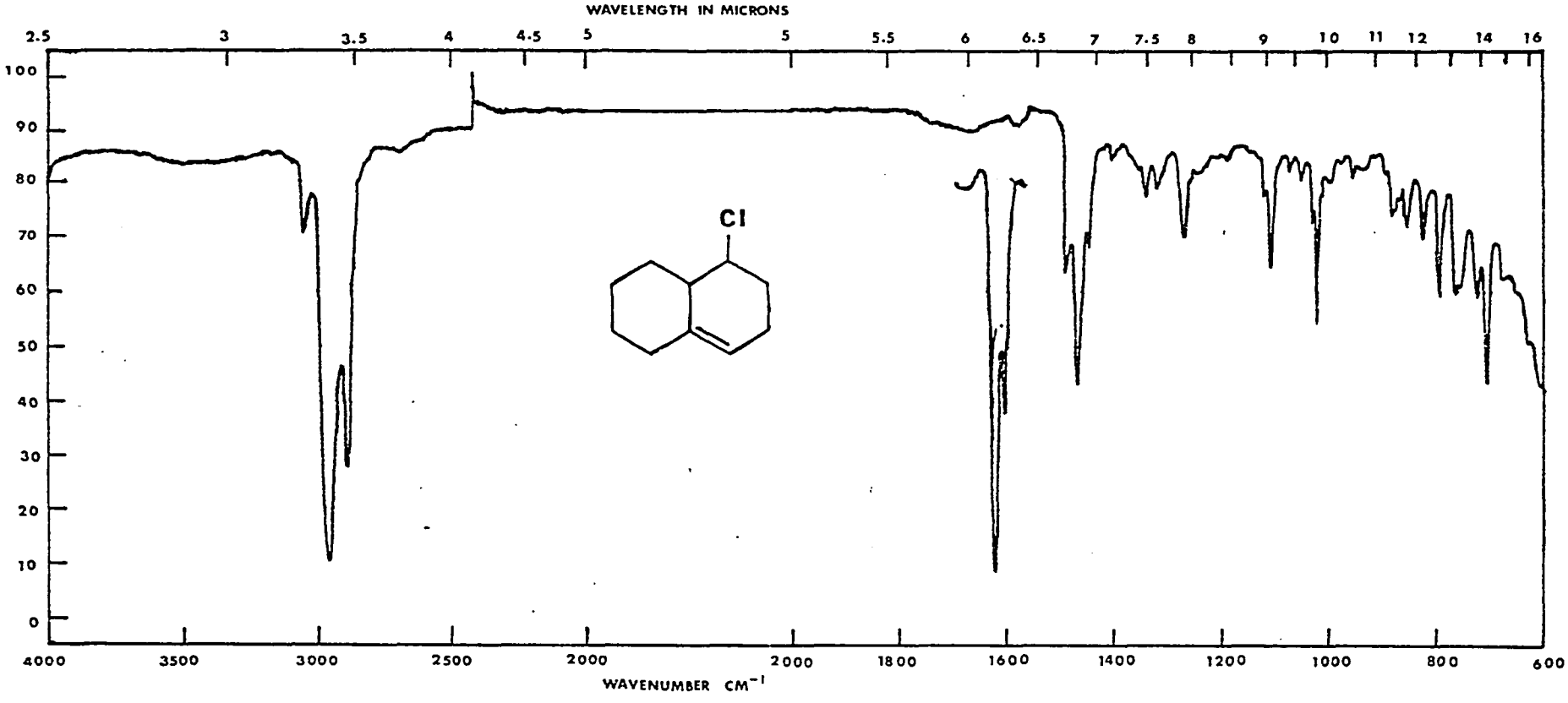

Figure 13. Infrared spectrum of 5-chlorobicyclo[4.4.0]dec-1-ene (XXII) (neat, sodium chloride plates).

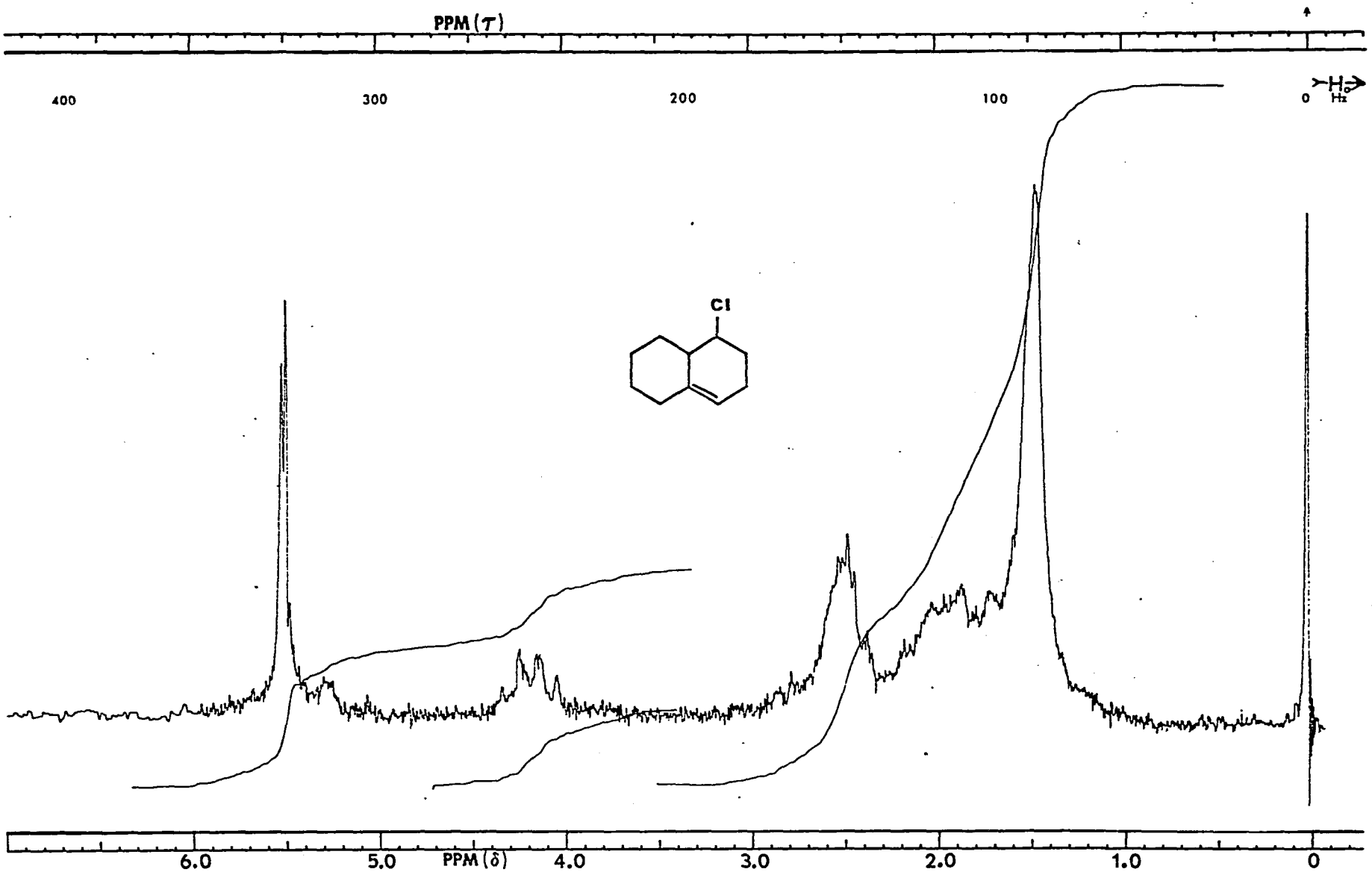

Figure 14. Nmr spectrum of 5-chlorobicyclo[4.4.0]dec-1-ene (XXII) in CCl_4 at 60 MHz.

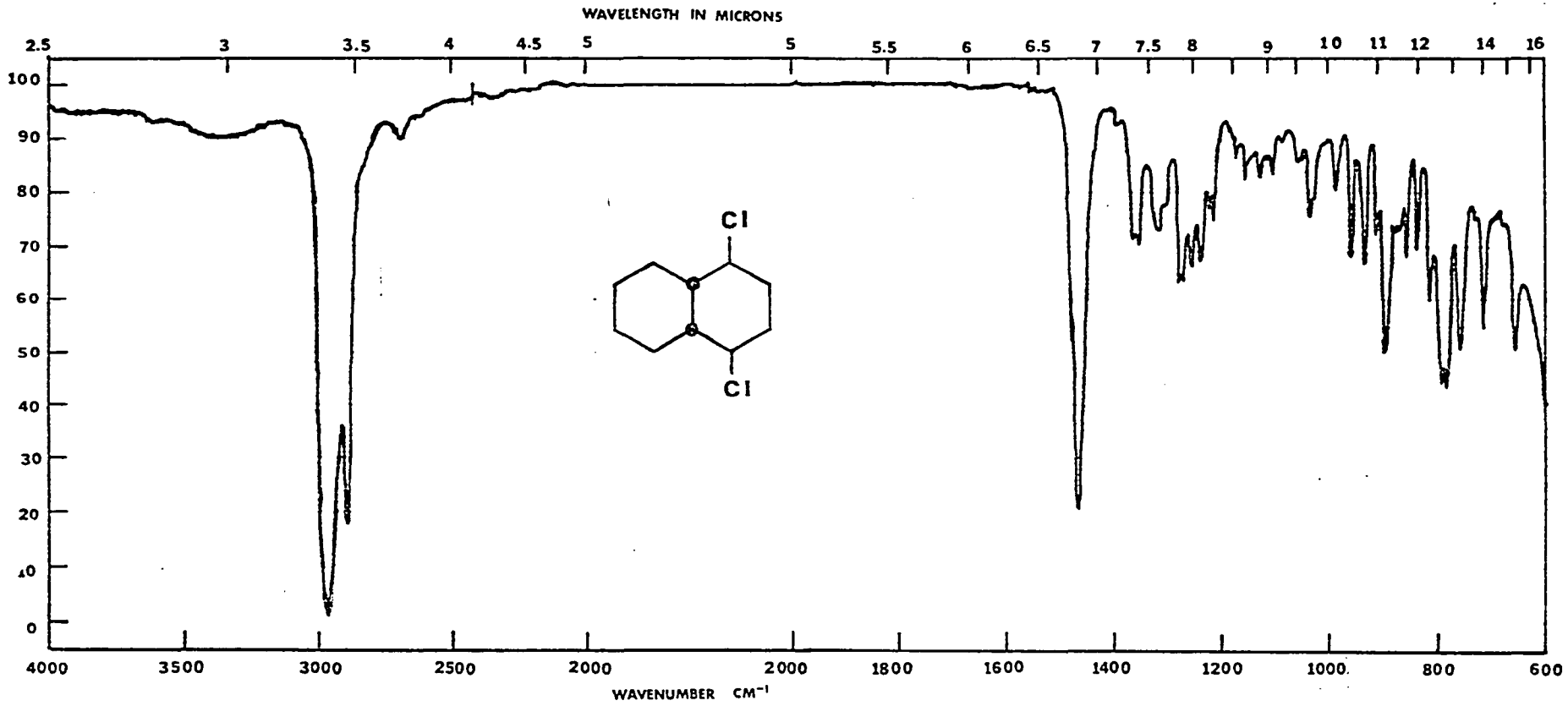

Figure 15. Infrared spectrum of 1,4-dichloro-cis-decalin (XXIII) (neat, sodium chloride plates).

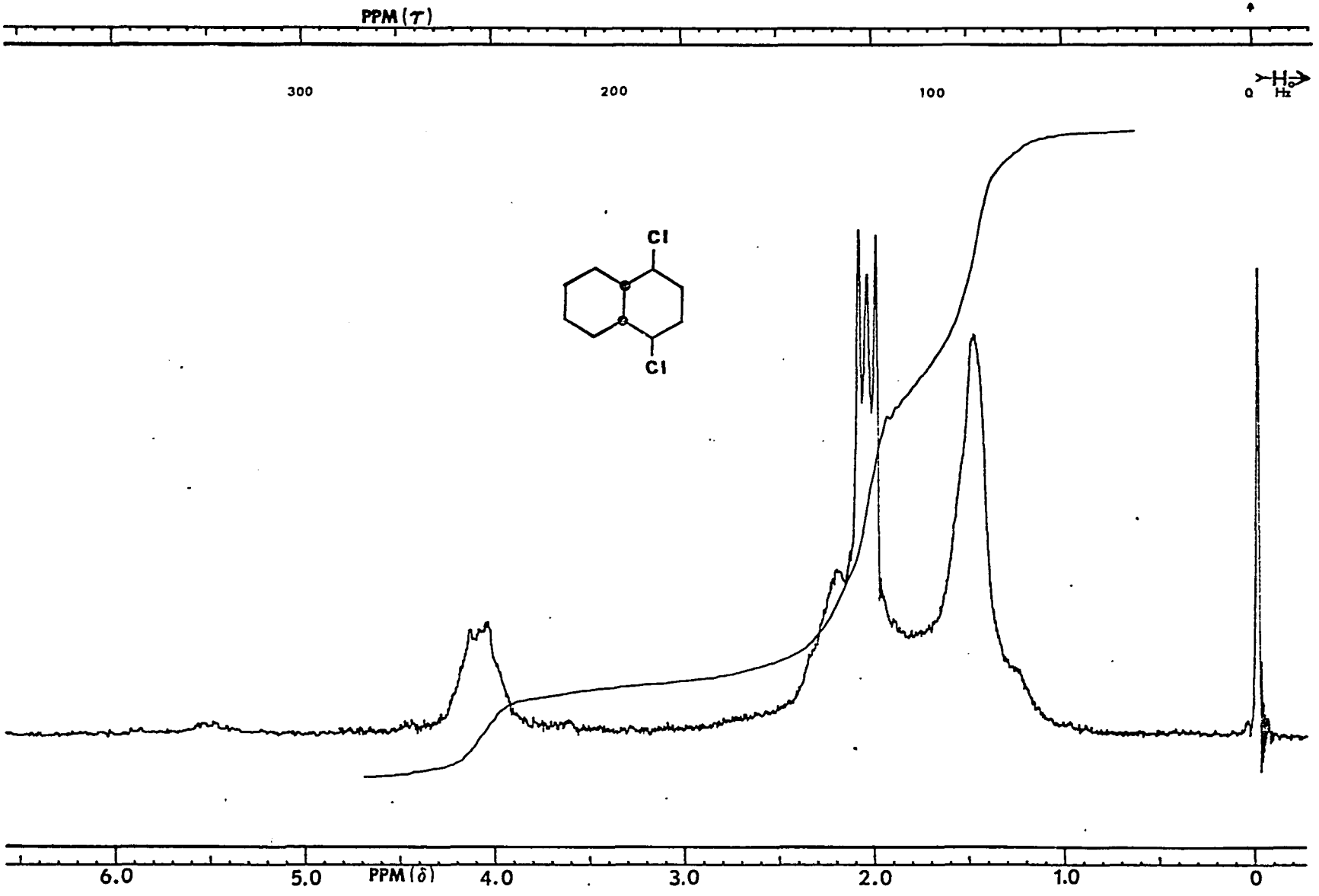

Figure 16. Nmr spectrum of 1,4-dichloro-cis-decalin (XXIII) in CCl_4 at 60 MHz.

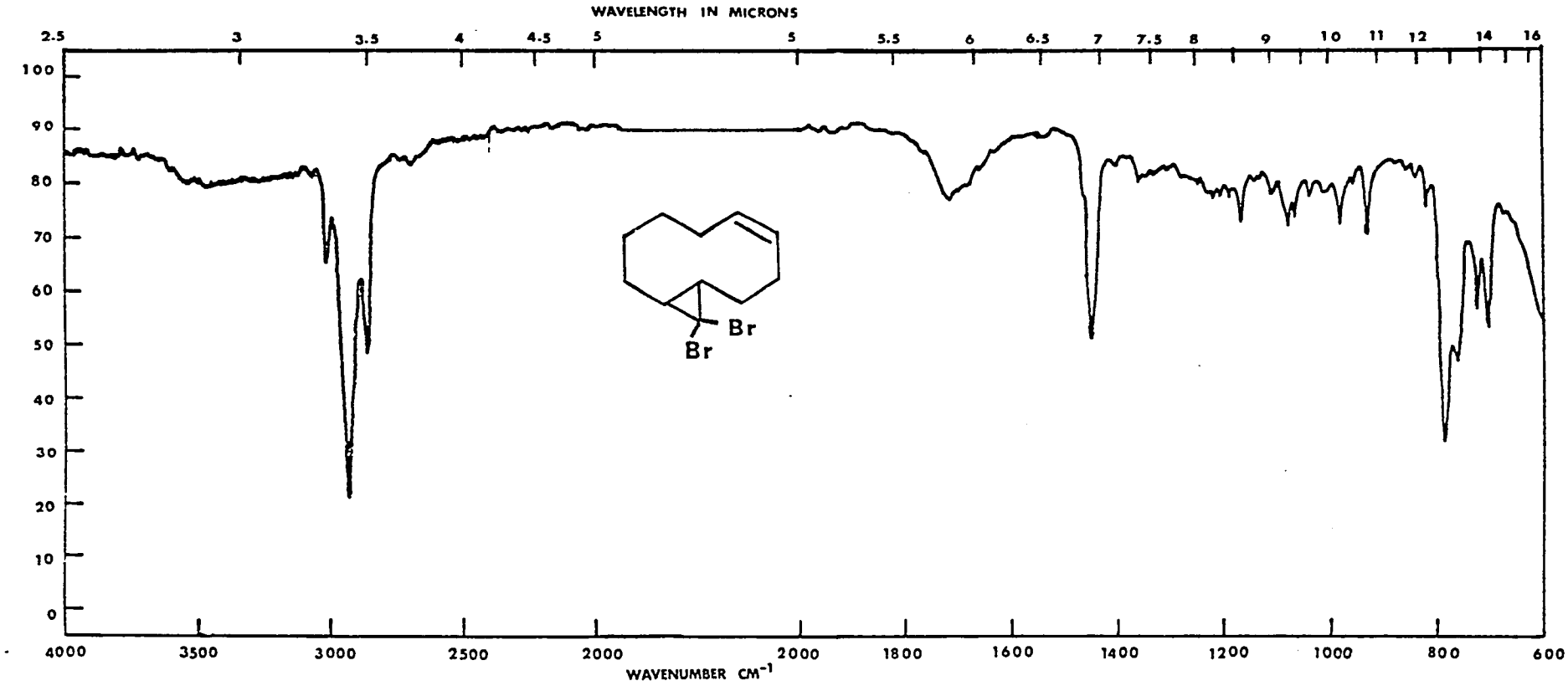

Figure 17. Infrared spectrum of 11,11-dibromobicyclo[8.1.0]-cis-5-undecene (XXVb) (neat, sodium chloride plates).

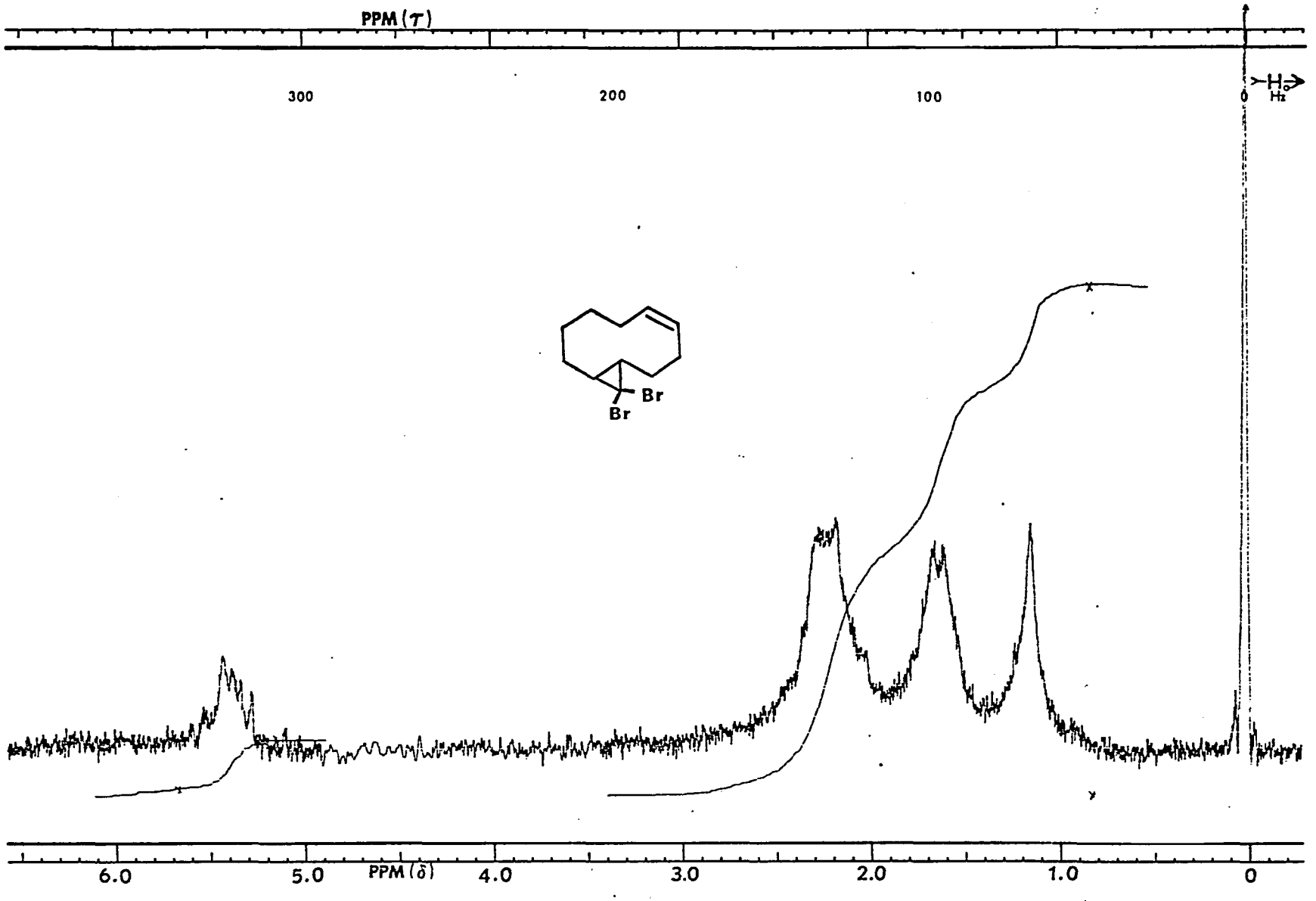

Figure 18. Nmr spectrum of 11,11-dibromobicyclo[8.1.0]-cis-5-undecene (XXVb) in CCl_4 at 60 MHz.

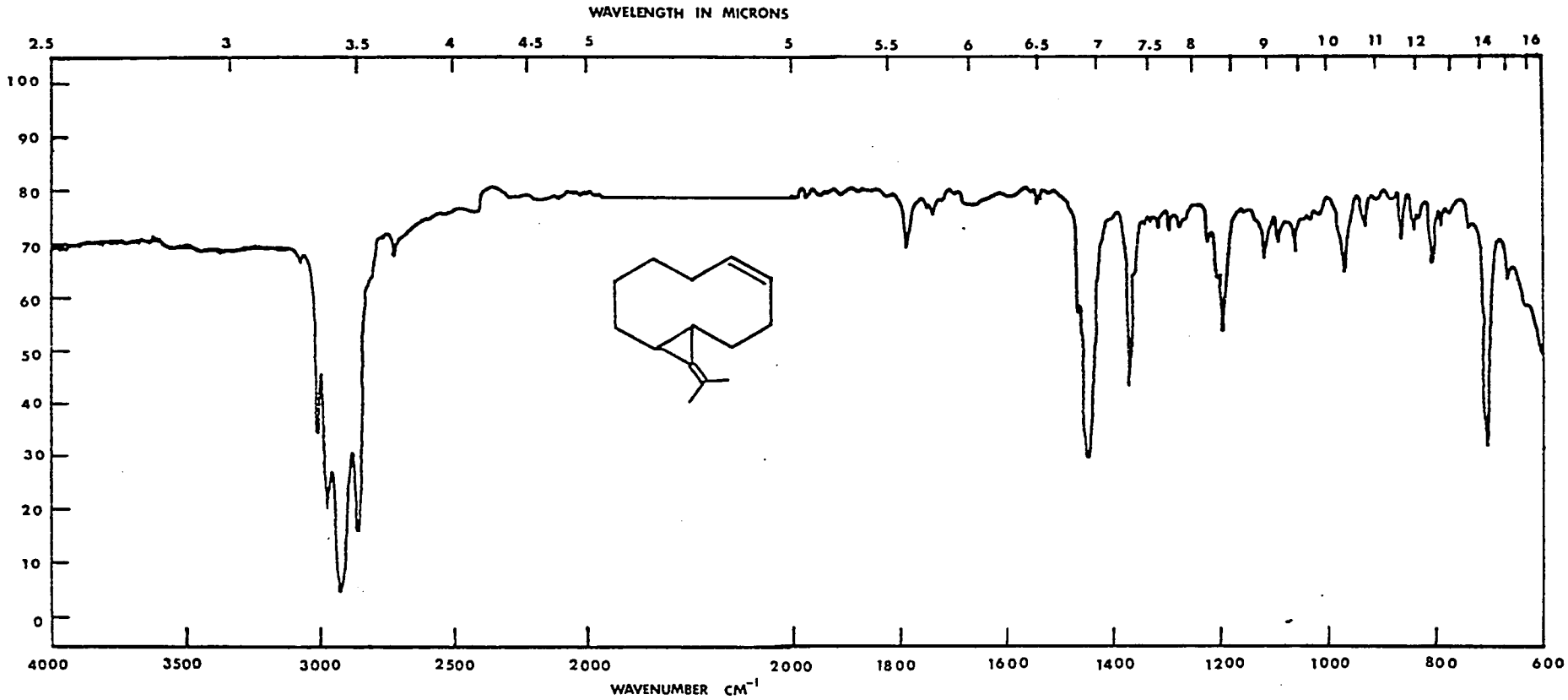

Figure 19. Infrared spectrum of 11-isopropylidenebicyclo[8.1.0]-cis-5-undecene (XXVc) (neat, sodium chloride plates).

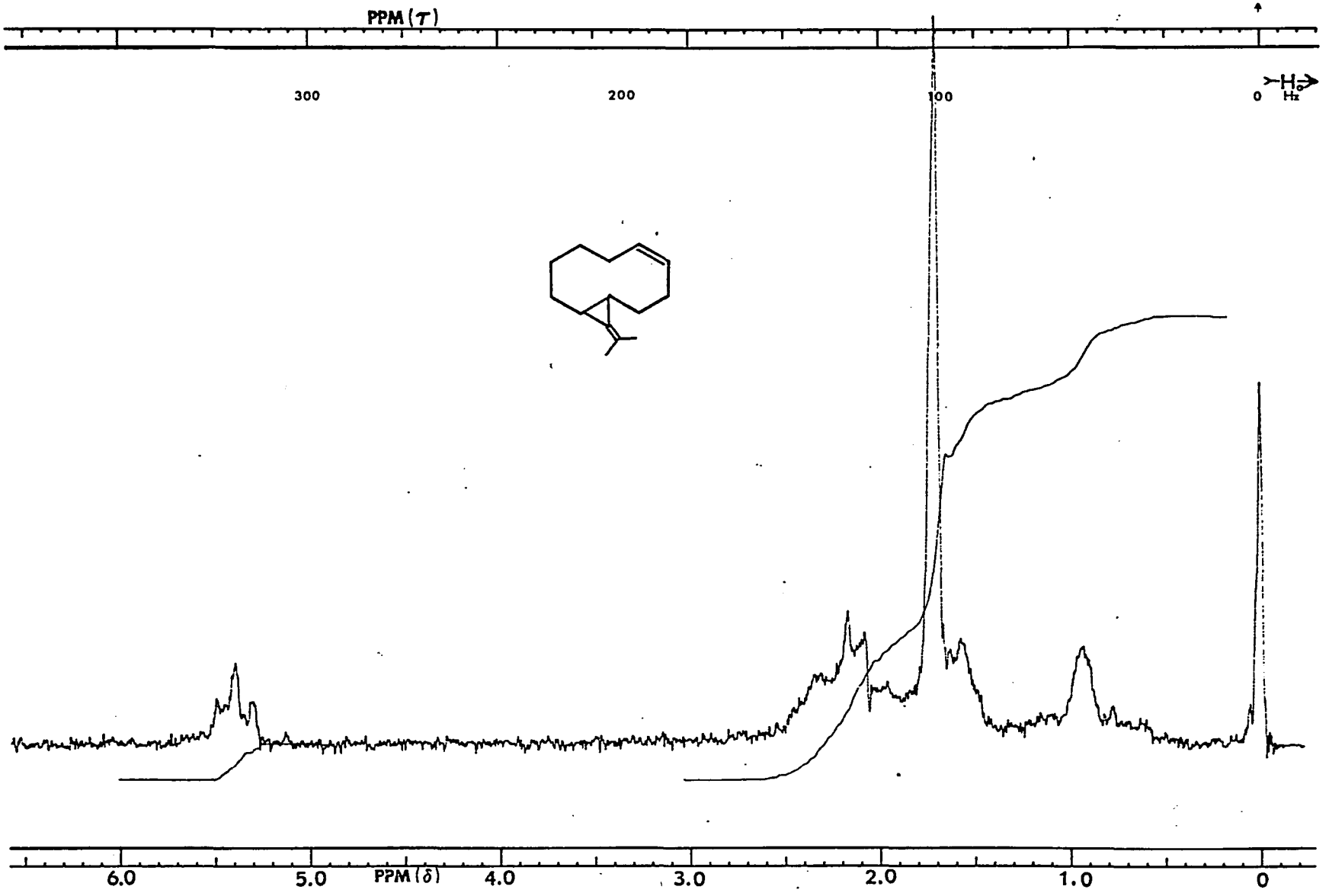

Figure 20. Nmr spectrum of 11-isopropylidenebicyclo[8.1.0]-cis-5-undecene (XXVc) in CCl_4 at 60 MHz.

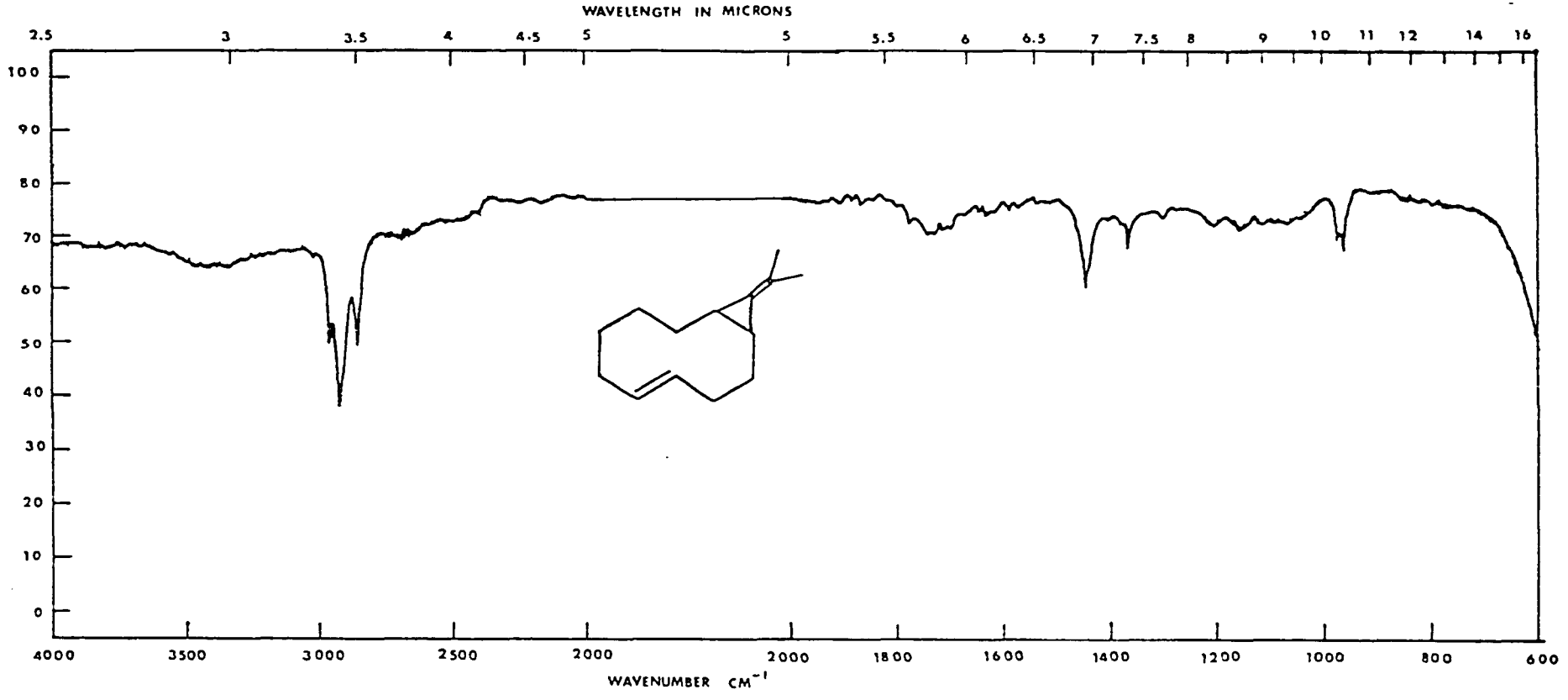

Figure 21. Infrared spectrum of 11-isopropylidenebicyclo[8.1.0]-trans-5-undecene (XXVIc) (neat, sodium chloride plates).

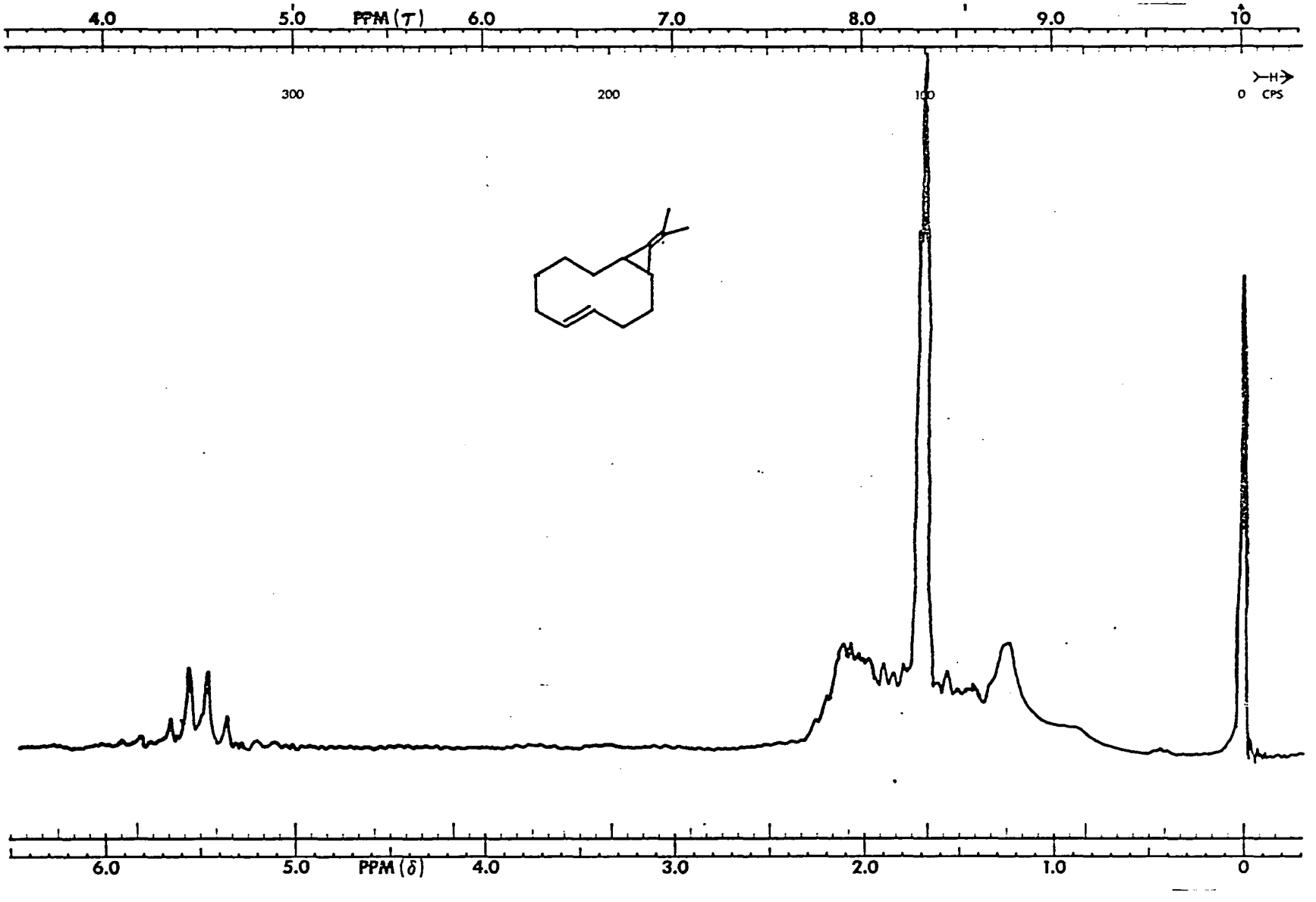

Figure 22. Nmr spectrum of 11-isopropylidenebicyclo[8.1.0]-trans-5-undecene (XXVIc) in CCl_4 at 60 MHz.

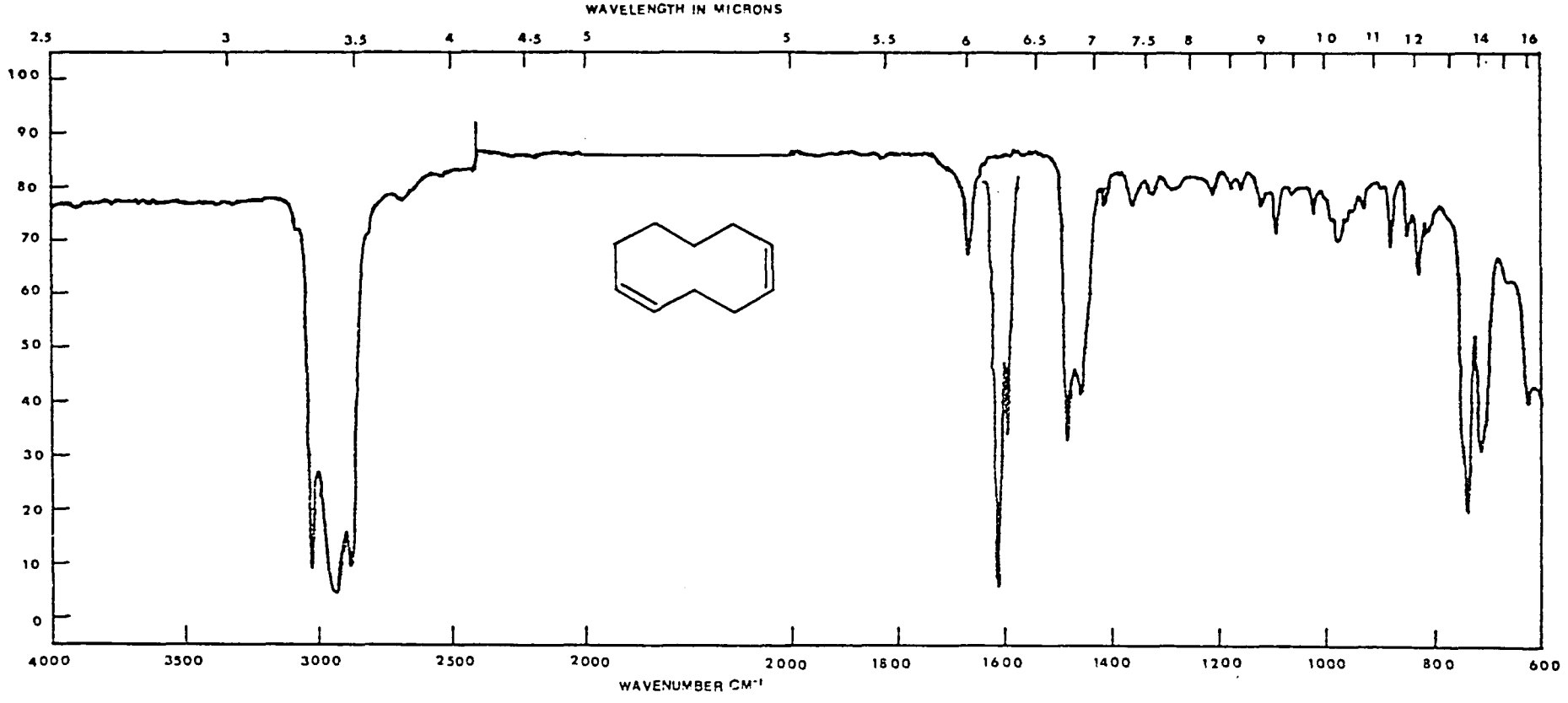

Figure 23. Infrared spectrum of cis,cis-1,5-cyclodecadiene (XLIII) (neat, sodium chloride plates).

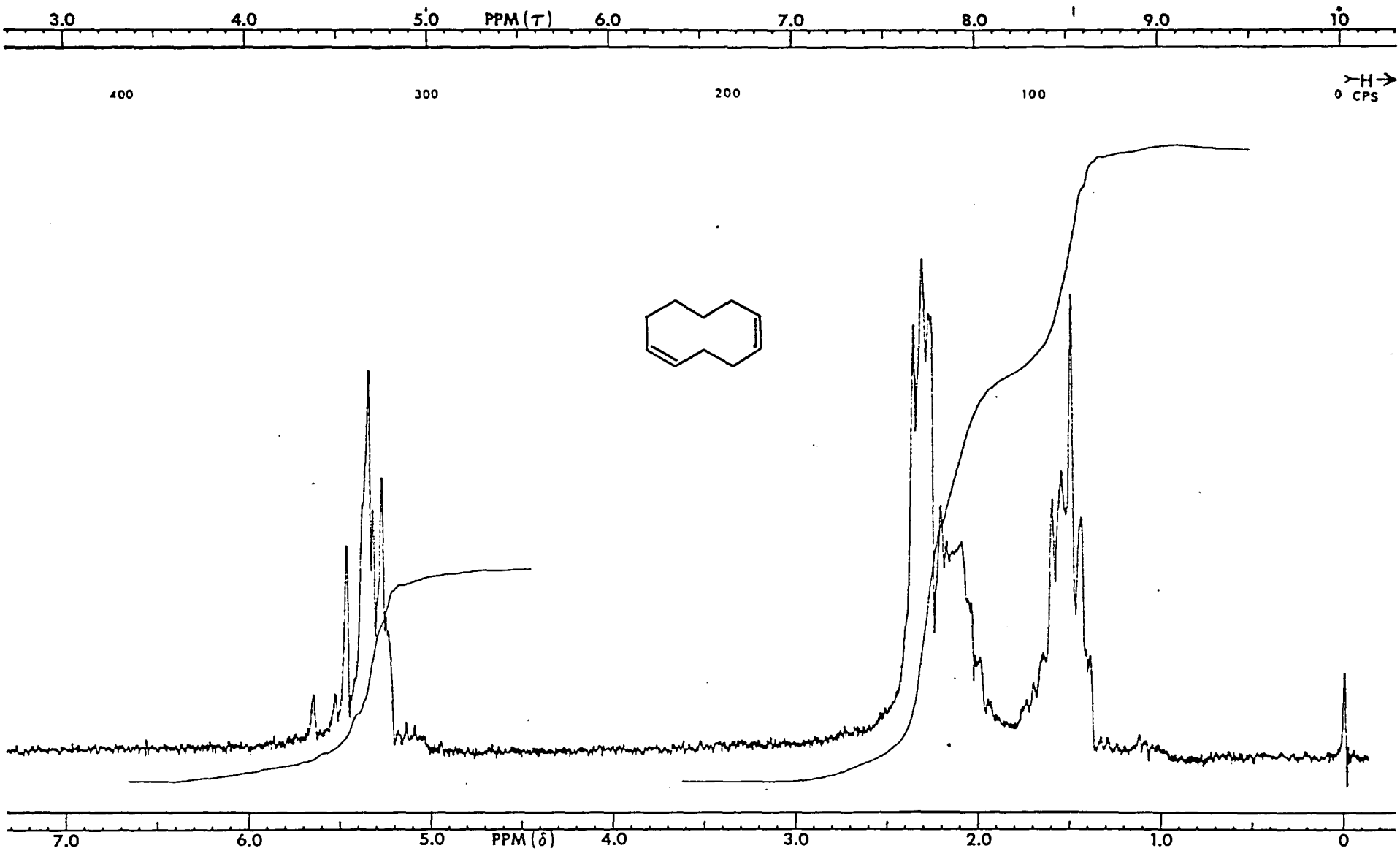

Figure 24. Nmr spectrum of cis,cis-1,5-cyclodecadiene (XLIII) in CCl_4 at 60 MHz.

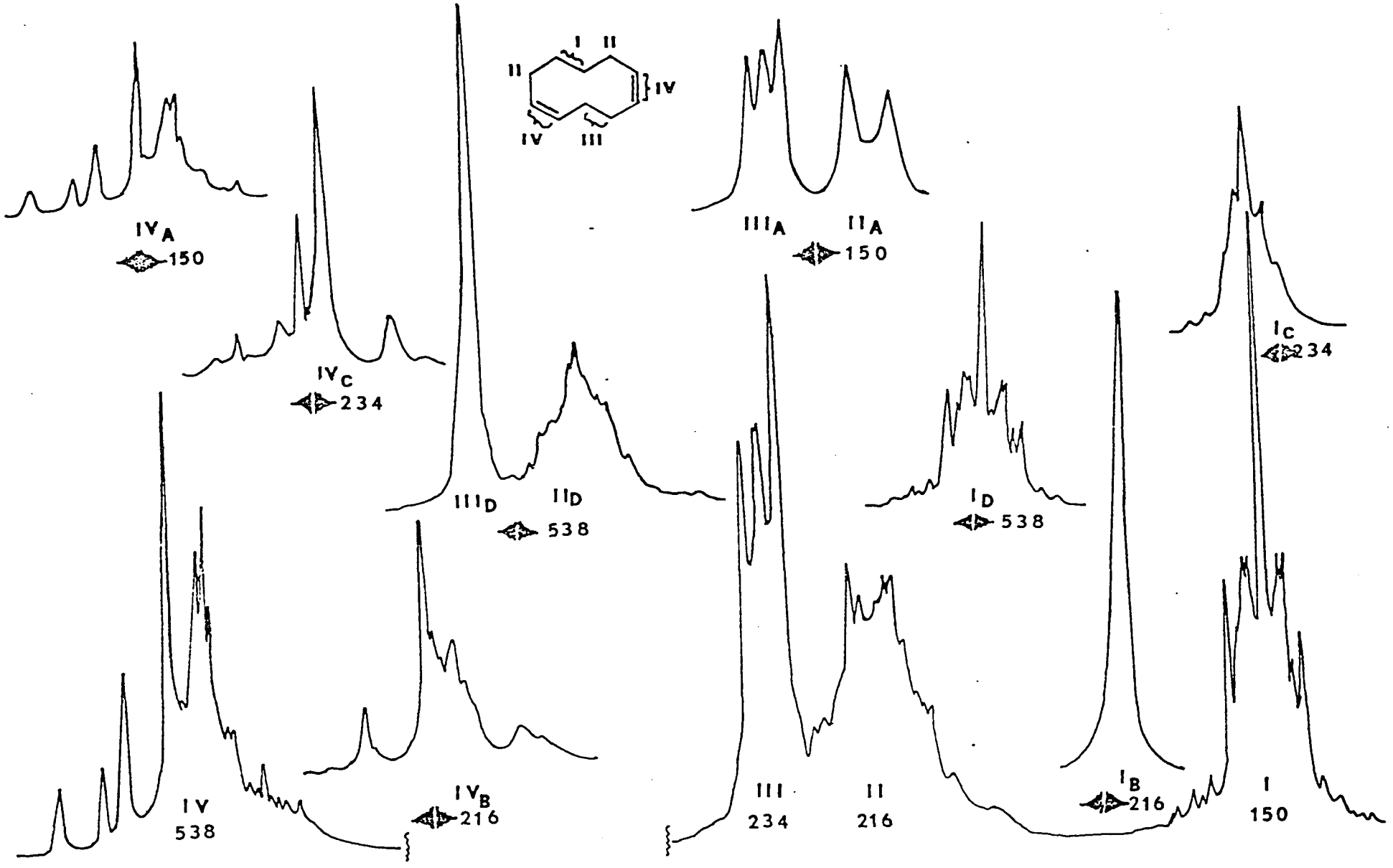

Figure 25. Decoupled nmr spectra of cis,cis-1,5-cyclodecadiene (XLIII) in $CDCl_3$ at 100 MHz.

VITA

Hsin-Hsiong Hsieh was born in Pingtung, Taiwan, China, on October 24, 1936. He graduated in 1955 from Taiwan Provincial Pingtung High School. He entered Taiwan Provincial Chung-Hsing University in Taichung, Taiwan, and obtained the B.S. degree in Chemistry in 1960. He entered the Graduate School of Louisiana State University in Baton Rouge, Louisiana in 1964, shortly after marrying Yi-Jong Chen. He received the M.S. degree in Biochemistry in 1966 and changed his major study to organic chemistry. He is presently a candidate for the degree of Doctor of Philosophy with a major in organic chemistry and a minor in biochemistry.

EXAMINATION AND THESIS REPORT

Candidate: Hsin-Hsiong Hsieh

Major Field: Chemistry

Title of Thesis: Addition Reactions and Photoisomerization of Cis,trans-1,5-Cyclodecadie

Approved:

James G. Traynham

Major Professor and Chairman

Max Yeadrick

Dean of the Graduate School

EXAMINING COMMITTEE:

Paul G. Gassman

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Joel Selbin

N S Bhacca

Date of Examination:

July 22, 1970